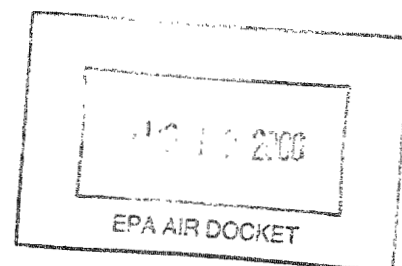


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Revised Final Report

**MODELING CUMULATIVE OUTDOOR
CONCENTRATIONS OF HAZARDOUS AIR
POLLUTANTS**

VOLUME I: TEXT

Systems Applications International, Inc.

February 1999

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ATTACHMENT 2 The Potential Importance of Agricultural Pesticide Volatilization

ATTACHMENT 3 HAP Profile Review and Development

ATTACHMENT 4 Sensitivity Analyses of ASPEN Dispersion and Mapping Modules

ATTACHMENT 5 Model Performance Evaluation

ATTACHMENT 6 Molecular Form of Emissions of Selected Pollutant Classes

ATTACHMENT 7 Effect of Neglecting Elevated Terrain

ATTACHMENT 8 Outdoor Concentration Estimates for 10 Metropolitan Statistical Areas

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PREFACE

Since the February 1998 version of this report was published, two data processing errors were identified in a number of locations. The first error caused incorrectly elevated mobile source emissions to be estimated for some census tracts. The second error was an incorrect application of calculation procedures in a number of census tracts that are small in area. These errors had little impact on overall results of the study, but have resulted in minor revisions to the summary data presented in a number of tables, primarily in Chapters 4 and 6.

In addition, concentration estimates for bis(2-ethylhexyl)phthalate (DEHP) have been revised. The units for the DEHP background concentration were misreported in the reference cited for the value (see Chapter 6). The correction of this error results in substantially reduced estimates of 1990 outdoor concentrations of this pollutant.

Finally, minor revisions have been made to the model performance evaluation presented in Chapter 7 and Attachment 5. These revisions reflect some corrections to the monitoring data set used in the evaluation, but do not affect the findings of the analysis.

1 INTRODUCTION

BACKGROUND

The U.S. Environmental Protection Agency's Cumulative Exposure Project is a broad-based examination of multiple pollutants in various environmental media. Individual components of the project address outdoor concentrations of air toxics, exposures to food contaminants, and exposures to drinking water contaminants. This report describes the modeling of outdoor air toxics concentrations conducted as part of the Cumulative Exposure Project.

Section 112 of the Clean Air Act (CAA), as amended in 1990, identifies 189 hazardous air pollutants (HAPs, also known as "air toxics") and mandates a variety of regulatory controls on sources of these pollutants. Many of these pollutants have been classified by EPA as known, probable or possible human carcinogens, and many are associated with other adverse human health effects detected in animal studies or occupational studies, such as reproductive effects, developmental effects, and neurological effects (EPA, 1994a). In contrast with the air pollutants known under the CAA as "criteria pollutants," such as ozone, particulate matter and carbon monoxide, little is known about the concentrations of HAPs in outdoor air or the national distribution of these concentrations. For most HAPs, the availability of measurement data is very limited. For example, Kelley et al. (1994) reported on a survey of ambient measurements of the 189 listed air toxics in populated areas of the US available from computerized data bases, published literature, and unpublished data from monitoring programs. The survey found fewer than 100 observations each for 116 HAPs (61%), with no ambient measurements for 74 of those HAPs. More than 1000 observations were found for only 42 of the 189 HAPs (22%). An observation was defined as one or more measurements at a single location within any 24-hour period between 1967 and 1992.

To gain a greater understanding of air toxics concentrations, this modeling study estimates 1990 long-term average outdoor concentrations of 148 air toxics nationally, by census tract, using existing methods and data. Outdoor concentrations of air toxics, resulting from emissions of these pollutants by both stationary and mobile sources, are an important indicator of potential health risks. Outdoor concentrations make a significant contribution to air toxics exposures, even though most individuals spend 80 percent or more of their time indoors (Robinson and Thomas, 1991; Johnson, 1987; Wiley et al., 1991a,b). This is due to the high rates of penetration of outdoor air toxics into indoor environments, seen in field sampling studies of indoor and outdoor concentrations of HAPs in gaseous form, and to a somewhat lesser extent, in particulate form (Lewis, 1991; Lewis and Zweidinger, 1992; Koutrakis et al., 1992; Ozkaynak et al., 1995). Long-term outdoor concentrations of air toxics in excess of "benchmark concentrations" (i.e., levels that may indicate a potential health hazard) are therefore an indicator of locations in which residents may be exposed to unhealthy levels of these pollutants.

Planned uses of the outputs of the modeling study include:

- Identification of priority HAPs for further attention;
- Estimating the relative contributions of broad categories of emissions sources—large stationary sources, small stationary sources, and mobile sources—to HAP concentrations;
- Characterizing the potential public health implications of air toxics, by comparing modeled concentrations to health benchmark concentrations drawn from the available toxicological data; and
- Characterizing the relationship between the geographic distribution of the modeled air toxics concentrations and demographic variables, such as race/ethnicity and income.

These analyses of the model outputs will be presented elsewhere. This report focuses on the dispersion modeling study itself, and includes descriptions of the modeling methodology, data inputs to the model, model outputs, and model performance evaluation. A previous draft report describing the modeling methodology (Rosenbaum et al., 1996) was reviewed by US EPA's Science Advisory Board (SAB, 1996).

SELECTION OF A MODELING APPROACH FOR ESTIMATING OUTDOOR CONCENTRATIONS OF HAPS

Selection of a modeling approach invariably involves tradeoffs in levels of detail that can be used in representing various operative atmospheric physical and chemical processes. The key is to identify which features are most critical to the modeling objective, and treat those features with greatest detail. No model can treat all aspects of atmospheric physics and chemistry at a state-of-the-science level.

A long-term Gaussian dispersion modeling approach was adopted for this study. This decision was based on the need for treatment of annual average concentrations and preservation of spatial concentration gradients. Although treatment of other important factors such as long-range transport, deposition, and atmospheric transformation are relatively crudely represented in this approach, even a crude representation is an improvement over existing exposure modeling studies, in which these processes may not be addressed at all.

The Human Exposure Model (HEM) (Anderson, 1983) was designed to model long-term concentrations over large spatial scales. Various versions of the HEM have been used by EPA staff repeatedly over the years to support regulatory activity (e.g., EPA, 1995e). The HEM utilizes a Gaussian dispersion modeling approach for point sources with optional first-order decay and a simple deposition algorithm. In the original version, area sources may be represented either by a "box" model or by multiple, geographically dispersed, prototype point sources. Concentrations resulting from any number of sources are extrapolated from model receptor locations to the centroids of population subdivisions, such as census tracts, block groups, or blocks. The model may be used to simulate any size modeling domain for which appropriate data are available.

A photochemical grid modeling approach was briefly considered for this study. However, modeling the entire contiguous United States would require the use of grid cells on the order

of 50 km. Essentially, most cities would be largely contained in a single grid cell, and spatial gradients arising from emissions from major point sources would not be captured. Existing regional-scale grid models such as the UAM-V have the capability to incorporate higher resolution in specific subdomains, but each added subdomain increases computing requirements. Resource requirements for adding all target HAPs to an existing photochemical model, developing a gridded national inventory, and exercising the model for a full year were prohibitive.

The grid modeling approach could be utilized with manageable resource requirements if a small number of representative geographic areas and time periods were selected and modeled with a high geographic resolution and the results extrapolated to other locations and time periods. The primary disadvantage of extrapolation in time or space is the uncertainty introduced by the required assumptions of similarity. The smaller the number of prototype time periods and/or locations, the greater the chance that pertinent differences between time periods and/or locations will be masked and estimates will be biased. This approach did not meet the study objectives of characterizing geographic variation in exposures.

SELECTION OF A MODELING SCENARIO

Since the goal of this study is to characterize outdoor concentrations in the vicinity of residential populations, a formulation that provides higher spatial resolution in areas of highest population density is desirable. In recognition of the potential for a large degree of spatial variation in ambient concentrations, the level of geographic resolution was selected to be the census tract level. There are approximately 60,000 census tracts in the United States. Census tracts contain roughly equal populations. Thus, they tend to be small in cities (90% $\leq 5 \text{ km}^2$) and larger in rural areas (median 50 km^2). This level of resolution represents a balance between the desire for high spatial resolution needed to address geographical variation in HAP concentrations, and the limitations of models and the available emissions and meteorological databases that preclude accurate modeling at higher resolution.

The year 1990 was selected as the base modeling period. It was selected because emissions and meteorological data were readily available, because it has been used as a base year in many other analyses, and because it represents a year prior to the implementation of any emission controls mandated by the 1990 amendments to the CAA.

The 48 conterminous United States was selected as the modeling domain. This decision was driven by the lack of data for Alaska and Hawaii in the emissions databases used.

The CAA list of 189 HAPs was selected as the initial list of target species. This list was modified somewhat due to data limitations, as described in Chapter 2.

DEVELOPMENT OF A NATIONAL-SCALE SET OF MODEL INPUT DATA

In order to apply the ASPEN model to estimate outdoor concentrations of HAPs at the resolution of census tracts, the following databases were developed.

- A national HAP emission inventory, stratified into 10 source categories—including manufacturing and nonmanufacturing stationary sources, and mobile sources—and resolved by census tract. The evaluation and selection of emissions data sources, and

the development of the inventory are described in Chapter 3. The results are described and compared to other inventories in Chapter 4.

- A database of meteorological data, including joint frequency distributions of wind speed, wind direction, and atmospheric stability at 214 meteorological stations, as well as temperature and precipitation data. In addition, annual average mixing heights, stratified by time of day were estimated for 63 sites.
- A database of information about the approximately 60,000 U.S. Census tracts in the conterminous U.S., including location, area, and urban or rural characterization.

STRUCTURE OF THE REPORT

This report contains seven chapters. Chapter 2 describes the results of some HAP characterization analyses used to select and characterize target HAPs. Chapters 3 and 4 describe the development and assessment of the national HAP emission inventory, including the data sources used. Chapter 5 describes the formulation, specifications, and uncertainties in the portion of the ASPEN modeling system used for the estimation of outdoor concentrations. Chapter 6 summarizes the HAP concentration estimates resulting from the modeling simulations. Chapter 7 describes the model performance evaluation procedures and summarizes the results. In addition, there are seven attachments, bound under separate cover, which provide additional detail for some of the issues and analyses discussed in the main body of the report.

2 CHARACTERIZATION OF HAPS

The 189 listed HAPs cover such a diversity of chemicals that some background investigation was required to determine how best to model ambient HAP concentrations and inhalation exposures. Three brief characterization analyses were conducted:

- Physical/chemical characterization, including chemical formula, physical form, and atmospheric reactivity
- Source characterization
- Ambient concentration characterization

These analyses relied primarily on recent data compilations and reviews, and were not comprehensive literature searches. Their purpose was to determine which of the listed HAPs could be modeled, the relevant physical and chemical processes for each, and the availability of ambient data against which the model results could be compared.

This section describes two of the HAP characterization studies: physical/chemical characterization and ambient concentration characterization. Using information from these analyses and the source characterization, the set of species modeled in the ambient portion of this study were selected.

PHYSICAL/CHEMICAL CHARACTERIZATION

In Table 2-1, the physical and chemical characteristics of the listed HAPs are summarized. The chemical formula and Chemical Abstracts (CAS) number are provided for each entry that is a pure compound in order to uniquely identify it. Each entry is identified as organic or inorganic (O/I). The physical form of the HAP in the atmosphere is identified as gas phase (G) or particulate (P). Many of the semivolatile organic compounds can exist in both phases in the atmosphere; these are designated G/P. The atmospheric reactivity of each HAP (i.e., how quickly it is removed through chemical transformation) is categorized as high (H), medium (M), low (L), or very low (VL). Finally, those HAPs that are known to be formed in the atmosphere through secondary reactions are identified. Species that could be formed in the atmosphere through secondary reactions are identified as possible (P).

Two recent EPA-sponsored studies (Kao, 1994; Kelly et al., 1994) were used as the primary resources for the development of Table 2-1. Additional data sources include the Merck index (Merck, 1983), the Handbook of Environmental Fate and Exposure Data, volumes I through IV (Howard, 1989, 1990, 1991, 1992), the NIST Chemical Kinetics Database, version 4 (NIST, 1992), recent reviews of atmospheric reactivity of HAPs (Grosjean, 1990a,b,c, 1991a,b,c), and personal communication (Miller, 1997). Atmospheric reactivity for some HAPs was estimated using the methodology of Atkinson (1986).

For the purposes of the approximate rank ordering of HAP reactivity presented in Table 2-1, typical annual-average conditions are taken to be: OH radical concentration of 0.05 ppt, or

TABLE 2-1. Physical and chemical properties of hazardous air pollutants (HAPs). G/P = gas/particulate phase; O/I = organic/inorganic; reactivity = H (high), M (medium), L (low), VL (very low); secondary = Y (formed by secondary atmospheric reactions), P (possibly formed in secondary atmospheric reactions).

HAP	Formula	CAS No.	G/P	O/I	Reactive	Secondary
Acetaldehyde	CH ₃ CHO	75070	G	O	M	Y
Acetamide	CH ₃ CONH ₂	60355	G	O	H	P
Acetonitrile (methyl cyanide)	CH ₃ CN	75058	G	O	VL	
Acetophenone	C ₆ H ₅ COCH ₃	98862	G	O	L	P
Acetylaminofluorene(2)	C ₁₃ H ₉ NH ₂ COCH ₃	53963	G/P	O	H	
Acrolein	CH ₂ CHCHO	107028	G	O	M	Y
Acrylamide	CH ₂ CHCONH ₂	79061	G	O	H	
Acrylic acid	CH ₂ CHCO ₂ H	79107	G	O	M	P
Acrylonitrile	CH ₂ CHCN	107131	G	O	L	
Allyl chloride (3-chloro-1-propene)	CH ₂ CHCH ₂ Cl	107051	G	O	M	
Aminobiphenyl(4)	C ₆ H ₅ C ₆ H ₄ NH ₂	92671	G	O	H	
Aniline	C ₆ H ₅ NH ₂	62533	G	O	H	
Anisidine(o) (methoxyaniline)	C ₆ H ₄ NH ₂ OCH ₃	90040	G	O	H	
Antimony Compounds	Sb	7440360	G/P	I	L	
Arsenic Compounds (inorganic including arsine)	As	7440382	G/P	I	L	
Asbestos	Mg(Si ₄ O ₁₀)(OH) ₈ (chrysotile)	1332214	P	I	L	
Benzene	C ₆ H ₆	71432	G	O	L	
Benzidine (diaminobiphenyl)	(C ₆ H ₄ NH ₂) ₂	92875	G/P	O	H	
Benzotrichloride	C ₆ H ₅ CCl ₃	98077	G	O	L	
Benzyl chloride	C ₆ H ₅ CH ₂ Cl	100447	G	O	L	
Beryllium Compounds	Be	7440417	P	I	L	
Biphenyl	C ₁₂ H ₁₀	192524	G	O	L	
Bis(2-ethylhexyl)phthalate (DEHP)	C ₂₄ H ₃₈ O ₄	117817	G/P	O	L	
Bis(chloromethyl)ether	C ₂ H ₄ Cl ₂ O	542881	G	O	L	
Bromoform	CHBr ₃	75252	G	O	VL	
Butadiene(1,3)	C ₄ H ₆	106990	G	O	H	
Cadmium Compounds	Cd	7440439	P	I	L	
Calcium cyanamide	CaCNN	156627	P	I	L	
Caprolactam	C ₆ H ₁₁ NO	105602	G	O	H	
Captan	C ₉ H ₈ Cl ₃ NO ₂ S	133062	G/P	O	H	
Carbaryl	C ₁₂ H ₁₁ NO ₂	63252	G/P	O	M	
Carbon disulfide	CS ₂	75150	G	O	L	
Carbon tetrachloride	CCl ₄	56235	G	O	VL	
Carbonyl sulfide	COS	463581	G	O	VL	Y
Catechol (1,2-benzenediol)	C ₆ H ₆ O ₂	120809	G	O	M	P
Chloramben	C ₇ H ₅ Cl ₂ NO ₂	133904	G	O	L	
Chlordane	C ₁₀ H ₆ Cl ₈	57749	G/P	O	VL	
Chlorine	Cl ₂	7782505	G	I	H	
Chloroacetic acid	ClCH ₂ COOH	79118	G	O	L	

Continued

TABLE 2-1. Continued.

HAP	Formula	CAS No.	G/P	O/I	Reactive	Secondary
Chloroacetophenone(2)	$\text{ClC}_6\text{H}_4\text{COCH}_3$	532274	G	O	L	
Chlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	108907	G	O	L	
Chlorobenzilate	$\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{O}_3$	510156	G/P	O	L	
Chloroform	CHCl_3	67663	G	O	VL	
Chloromethyl methyl ether	$\text{CH}_3\text{OCH}_2\text{Cl}$	107302	G	O	L	
Chloroprene (2-Chloro-1,3-butadiene)	$\text{C}_4\text{H}_5\text{Cl}$	126998	G	O	H	
Chromium Compounds	Cr	7440473	P	I	L	
Cobalt Compounds	Co	7440484	P	I	L	
Coke Oven Emissions	—	—	G/P	I/O	—	
Cresol(<i>m</i>)	$\text{C}_7\text{H}_7\text{OH}$	108394	G	O	H	Y
Cresol(<i>o</i>)	$\text{C}_7\text{H}_7\text{OH}$	95487	G	O	H	Y
Cresol(<i>p</i>)	$\text{C}_7\text{H}_7\text{OH}$	106445	G	O	H	Y
Cresols/Cresylic acid	$\text{C}_7\text{H}_7\text{OH}$	1319773	G	O	H	Y
Cumene (Isopropylbenzene)	C_9H_{12}	98828	G	O	L	
Cyanide Compounds	HCN	74908	G/P	I	L	
	NaCN	143339				
	KCN	151508				
D(2,4), salts and esters	$\text{C}_8\text{H}_6\text{Cl}_2\text{O}_3$	94757	G/P	O	L	
DDE	$\text{C}_{14}\text{H}_8\text{Cl}_4$	3547044	G/P	O	VL	Y
Diazomethane	CH_2N_2	334883	G	O	H	
Dibenzofurans	$\text{C}_{12}\text{H}_8\text{O}$	132649	G/P	O	L	
Dibromo-3-chloropropane(1,2)	$\text{C}_3\text{H}_5\text{ClBr}_2$	96128	G	O	L	
Dibutylphthalate	$\text{C}_{16}\text{H}_{18}(\text{COOC}_4\text{H}_9)_2$	84742	G/P	O	L	
Dichlorobenzene(1,4)(<i>p</i>)	$\text{C}_6\text{H}_4\text{Cl}_2$	106467	G	O	L	
Dichlorobenzidine(3,3)	$(\text{C}_6\text{H}_3\text{ClNH}_2)_2$	91941	G/P	O	M	
Dichloroethyl ether (Bis(2-chloroethyl)ether)	$(\text{ClCH}_2\text{CH}_2)_2\text{O}$	111444	G	O	M	
Dichloropropene(1,3)	$\text{C}_3\text{H}_4\text{Cl}_2$	542756	G	O	L	
Dichlorvos	$\text{C}_4\text{H}_7\text{Cl}_2\text{O}_4\text{P}$	62737	G	O	L	
Diethanolamine	$(\text{HOCH}_2\text{CH}_2)_2\text{NH}$	111422	G	O	H	
Diethyl aniline (N,N)	$\text{C}_6\text{H}_5\text{N}(\text{C}_2\text{H}_5)_2$	121697	G	O	H	
(Dimethylaniline (N,N))	$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$					
Diethyl sulfate	$(\text{C}_2\text{H}_5)_2\text{SO}_4$	64675	G	O	L	P
Dimethoxybenzidine(3,3) (Dianisidine)	$(\text{C}_6\text{H}_3\text{OCH}_3\text{NH}_2)_2$	119904	G/P	O	H	
Dimethyl aminoazobenzene	$\text{C}_6\text{H}_5\text{NNC}_6\text{H}_4\text{N}(\text{CH}_3)_2$	60117	G/P	O	H	
Dimethyl benzidine(3,3)	$(\text{C}_6\text{H}_3\text{CH}_3\text{NH}_2)_2$	119937	G/P	O	H	
Dimethyl carbamoyl chloride	$(\text{CH}_3)_2\text{NCOCI}$	79447	G	O	L	
Dimethyl formamide	$\text{HCON}(\text{CH}_3)_2$	68122	G	O	H	
Dimethyl hydrazine(1,1)	$(\text{CH}_3)_2\text{NNH}_2$	57147	G	O	H	
Dimethyl phthalate	$\text{C}_6\text{H}_4(\text{COOCH}_3)_2$	131113	G	O	L	
Dimethyl sulfate	$(\text{CH}_3)_2\text{SO}_4$	77781	G	O	L*	P
Dinitro- <i>o</i> -cresol(4,6), and salts	$\text{C}_7\text{H}_6\text{N}_2\text{O}_5$	534521	G/P	O	L	
Dinitrophenol(2,4)	$\text{C}_6\text{H}_3\text{OH}(\text{NO}_2)_2$	51285	G/P	O	M	P
Dinitrotoluene(2,4)	$\text{C}_7\text{H}_6(\text{NO}_2)_2$	121142	G	O	L	
Dioxane(1,4) (1,4-Diethyleneoxide)	$\text{C}_4\text{H}_8\text{O}$	123911	G	O	M	

Continued

TABLE 2-1. Continued.

HAP	Formula	CAS No.	G/P	O/I	Reactive	Secondary
Diphenylhydrazine(1,2)	(C ₆ H ₅) ₂ NNH ₂	122667	G	O	H	
Epichlorohydrin (Chloro-2,3-epoxy- propane(1))	C ₃ H ₅ ClO	106898	G	O	L	P
Epoxybutane(1,2) (1,2-Butylene oxide)	C ₄ H ₈ O	106887	G	O	L	P
Ethyl acrylate	C ₅ H ₈ O ₂	140885	G	O	M	
Ethylbenzene	C ₈ H ₁₀	100414	G	O	L	
Ethyl carbamate (Urethane)	C ₃ H ₇ NO ₂	51796	G	O	L	
Ethyl chloride (Chloroethane)	C ₂ H ₅ Cl	75003	G	O	L	
Ethylene dibromide (1,2-Dibromoethane)	C ₂ H ₄ Br ₂	106934	G	O	L	
Ethylene dichloride (1,2-Dichloroethane)	C ₂ H ₄ Cl ₂	107062	G	O	L	
Ethylene glycol	HOC ₂ H ₄ OH	107211	G	O	L	
Ethylene imine (Aziridine)	C ₂ H ₅ N	151564	G	O	H	
Ethylene oxide	C ₂ H ₄ O	75218	G	O	L	
Ethylene thiourea	C ₃ H ₆ N ₂ S	96457	G	O	H	
Ethylidene dichloride (1,1-Dichloroethane)	C ₂ H ₄ Cl ₂	75343	G	O	L	
Formaldehyde	HCHO	50000	G	O	M	Y
Glycol ethers (Cellosolves)	HOC _x H _{2x} OC _y H _{2y-1}	—	G	O	M	
Heptachlor	C ₁₀ H ₅ Cl ₇	76448	G/P	O	M	
Hexachlorobenzene	C ₆ Cl ₆	118741	G	O	VL	
Hexachlorobutadiene	C ₄ Cl ₆	87683	G	O	L	
Hexachlorocyclopentadiene	C ₅ Cl ₆	77474	G	O	L*	
Hexachloroethane	C ₂ Cl ₆	67721	G	O	VL	
Hexamethylene-1,6- diisocyanate	C ₆ H ₁₀ (CNO) ₂	822060	G/P	O	L	
Hexamethylphosphoramide	C ₆ H ₁₈ N ₃ OP	680319	G	O	L	
Hexane	C ₆ H ₁₄	110543	G	O	L	
Hydrazine	(NH ₂) ₂	302012	G	I	H	
Hydrochloric acid	HCl	7647010	G	I	L	Y
Hydrogen fluoride (Hydrofluoric acid)	HF	7664393	G	I	L	
Hydroquinone (1,4-benzenediol)	C ₆ H ₄ (OH) ₂	123319	G	O	M	
Isophorone	C ₉ H ₁₄ O	78591	G	O	H	
Lead Compounds	Pb	7439921	P	I	L	
Lindane (all isomers)	C ₆ H ₆ Cl ₆	58899	G/P	O	L	
Maleic anhydride (Furandione)	C ₄ H ₂ O ₃	108316	G	O	H	Y
Manganese Compounds	Mn	7439965	P	I	L	
Mercury Compounds	Hg	7439976	G/P	I	L	
Methanol	CH ₃ OH	67561	G	O	L	Y
Methoxychlor	CCl ₃ CH(C ₆ H ₄ OCH ₃) ₂	72435	G/P	O	L	
Methyl bromide (Bromomethane)	CH ₃ Br	74839	G	O	VL	

Continued

TABLE 2-1. Continued.

HAP	Formula	CAS No.	G/P	O/I	Reactive	Secondary
Methyl chloride (Chloromethane)	CH ₃ Cl	74873	G	O	VL	
Methyl chloroform (1,1,1-Trichloroethane)	C ₂ H ₃ Cl ₃	71556	G	O	VL	
Methyl ethyl ketone (2-Butanone)	C ₄ H ₈ O	78933	G	O	L	Y
Methyl hydrazine	CH ₃ NHNH ₂	60344	G	O	H	
Methyl iodide (Iodomethane)	CH ₃ I	74884	G	O	L	
Methyl isobutyl ketone (Hexone)	C ₆ H ₁₂ O	108101	G	O	M	Y
Methyl isocyanate	CH ₃ NCO	624839	G	O	M	
Methyl methacrylate	C ₃ H ₅ COOCH ₃	80626	G	O	H	
Methyl <i>tert</i> -butyl ether	C ₅ H ₁₂ O	1634044	G	O	L	
Methylene bis(2-chloroaniline)(4,4)	C ₁₃ H ₁₂ N ₂ Cl ₂	101144	G/P	O	H	
Methylene chloride (Dichloromethane)	CH ₂ Cl ₂	75092	G	O	L	
Methylene diphenyl diisocyanate (MDI)	CH ₂ (C ₆ H ₄ NCO) ₂	101688	G/P	O	M	
Methylenedianiline(4,4)	C ₁₃ H ₁₄ N ₂	101779	G/P	O	M	
Mineral fibers	—	—	P	I	L	
Naphthalene	C ₁₀ H ₈	91203	G	O	M	
Nickel Compounds	Ni	—	P	I	L	
Nitrobenzene	C ₆ H ₅ NO ₂	98953	G	O	M	Y
Nitrobiphenyl(4)	C ₁₂ H ₉ NO ₂	92933	G	O	L	
Nitrophenol(4)	C ₆ H ₅ OHNO ₂	100027	G	O	L	P
Nitropropane(2)	C ₃ H ₇ NO ₂	79469	G	O	L	
N-nitroso-N-methylurea	NH ₂ CON(CH ₃)NO	684935	G	O	H	
Nitrosodimethylamine(N)	(CH ₃) ₂ NNO	62759	G	O	H	Y
Nitrosomorpholine(N)	C ₄ H ₈ N ₂ O ₂	59892	G	O	H	Y
Parathion	C ₁₀ H ₁₄ NO ₃ PS	56382	G/P	O	H	
Pentachloronitrobenzene (Quintobenzene)	C ₆ Cl ₅ NO ₂	82688	G/P	O	L	
Pentachlorophenol	C ₆ Cl ₅ OH	87865	G/P	O	L	
Phenol	C ₆ H ₅ OH	108952	G	O	M	Y
Phenylenediamine(<i>p</i>)	C ₆ H ₅ (NH ₂) ₂	106503	G	O	H	
Phosgene	CCl ₂ O	75445	G	O	L	Y
Phosphine	H ₃ P	7803512	G	I	M	
Phosphorus	P	7723140	G/P	I	L	
Phthalic anhydride	C ₈ H ₄ O ₃	85449	G	O	L	
Polychlorinated biphenyls (PCB)	C ₁₂ Cl _x H _(10-x)	1336363	G/P	O	VL	
Polycyclic organic matter (POM)	—	—	G/P	O	L	
Propane sultone(1,3)	HSO ₃ C ₃ H ₆ OH	1120714	G	O	H	P
Propiolactone(beta)	C ₃ H ₄ O ₂	57578	G	O	L	
Propionaldehyde	C ₂ H ₅ CHO	123386	G	O	M	Y
Propoxur (Baygon)	C ₁₁ H ₁₅ NO ₃	114261	G/P	O	M	

Continued

TABLE 2-1. Concluded.

HAP	Formula	CAS No.	G/P	O/I	Reactive	Secondary
Propylene dichloride (1,2-Dichloropropane)	C ₃ H ₆ Cl ₂	78875	G	O	L	
Propylene oxide	C ₃ H ₆ O	75569	G	O	L	
Propylenimine(1,2) (2-Methyl aziridine)	C ₃ H ₈ N	75558	G	O	H	
Quinoline	C ₉ H ₇ N	91225	G	O	M	
Quinone (1,4-Cyclohexadienedione)	C ₆ H ₄ O ₂	106514	G	O	H	P
Radionuclides (including radon)	—	—	G/P	I	L	
Selenium Compounds	Se	7782492	P	I	L	
Styrene	C ₈ H ₈	100425	G	O	H	
Styrene oxide	C ₈ H ₆ O	96093	G	O	L	
Tetrachlorodibenzo- <i>p</i> - dioxin(2,3,7,8)	C ₁₂ H ₄ O ₂ Cl ₄	1746016	G/P	O	L	
Tetrachloroethane(1,1,2,2)	C ₂ H ₂ Cl ₄	79345	G	O	VL	
Tetrachloroethylene (Perchloroethylene)	C ₂ Cl ₄	127184	G	O	L	
Titanium tetrachloride	TiCl ₄	7550450	P	I	H	
Toluene	C ₇ H ₈	108883	G	O	L	
Toluene diamine(2,4) (2,4-Diaminotoluene)	C ₇ H ₁₀ N ₂	95807	G	O	H	
Toluene diisocyanate(2,4)	C ₉ H ₆ N ₂ O ₂	584849	G	O	L	
Toluidine(<i>o</i>)	C ₇ H ₉ N	95534	G	O	H	
Toxaphene (Chlorinated camphene)	mixture ~ C ₁₀ H ₁₀ Cl ₈	8001352	G/P	O	L	
Trichlorobenzene(1,2,4)	C ₆ H ₃ Cl ₃	120821	G	O	L	
Trichloroethane(1,1,2)	C ₂ H ₃ Cl ₃	79005	G	O	L	
Trichloroethylene	C ₂ HCl ₃	79016	G	O	L	
Trichlorophenol(2,4,5)	C ₆ H ₂ OHCl ₃	95954	G	O	L	P
Trichlorophenol(2,4,6)	C ₆ H ₂ OHCl ₃	88062	G	O	L	
Triethylamine	(C ₂ H ₅) ₃ N	121448	G	O	H	
Trifluralin	C ₁₃ H ₁₆ F ₃ N ₃ O ₄	1582098	G/P	O	H	
Trimethylpentane(2,2,4)	C ₈ H ₁₈	540841	G	O	L	
Vinyl acetate	C ₄ H ₆ O ₂	108054	G	O	M	
Vinyl bromide	C ₂ H ₃ Br	593602	G	O	L	
Vinyl chloride	C ₂ H ₃ Cl	75014	G	O	L	
Vinylidene chloride (1,1-Dichloroethylene)	C ₂ H ₂ Cl ₂	75354	G	O	M	
Xylene(<i>m</i>)	C ₈ H ₁₀	108383	G	O	M	
Xylene(<i>o</i>)	C ₈ H ₁₀	95476	G	O	M	
Xylene(<i>p</i>)	C ₈ H ₁₀	106423	G	O	M	
Xylenes (mixed)	C ₈ H ₁₀	1330207	G	O	M	

* Although this represents our best estimate of the atmospheric reactivity of this compound, higher estimates of reactivity have been presented in the literature.

1.2×10^6 molecules/cm³; an ozone concentration of 0.06 ppm; and typical tropospheric photolysis conditions. These OH and O₃ concentrations correspond to the mid-range for rural and the low end of moderately polluted air, according to Finlayson-Pitts and Pitts (*Atmospheric Chemistry*, 1986).¹ Species identified as highly reactive in Table 2-1 have atmospheric lifetimes of less than 6 hours under the specified typical annual-average conditions. Those identified as medium-reactivity have a lifetime between 6 and 24 hours; low-reactivity species have lifetimes between 1 and 60 days, and very low reactivity species have lifetimes greater than 60 days. Particulate species were all assumed to be low reactivity, based on an average lifetime due to deposition of greater than one day for fine particles.

Of the 189 HAPs, 132 are classified in Table 2-1 as organic compounds that will be present in the atmosphere in the gas phase (volatile organic compounds or VOCs). An additional 33 are organic compounds that may be present in both the gas and particulate phases (semivolatile organic compounds or SVOCs). Five are gas-phase inorganic compounds, six are inorganic species that can be present in both the gas and particulate phases, and 12 are particulate inorganic compounds (mainly metals). One (coke oven emissions) has components that are organic and inorganic, gaseous and particulate.

Of the listed HAPs, 46 are identified as or estimated to be highly reactive, 32 have medium reactivity, 96 have low reactivity, and 14 have very low reactivity. It should be noted that these lifetimes are annual averages. Under summer, daylight conditions, atmospheric lifetimes can be much shorter. Conversely, under winter conditions the lifetimes can be longer. It is also important to note that for some "group" entries (such as polycyclic organic matter, or POM), individual compounds can be very reactive, but the products of the reactions also fall within the same group entry definition. These group entries are generally classified as low reactivity based on removal rates for the group as a whole.

For the species listed as highly reactive, reactivity significantly decreases ambient concentrations. These species exist in the atmosphere only close to their sources. As the reactivity decreases, reactive losses have less of an effect on concentrations, but long-range transport becomes an increasingly important factor. For the HAPs with very low reactivity, an anthropogenic background concentration exists that is the cumulative effect of global emissions.

Twenty of the listed HAPs are known to be formed in the atmosphere. Another 13 may be formed in the atmosphere, or are formed in known but small quantities. The precursors for these secondary HAPs are summarized in Table 2-2. Many of the secondary HAPs have major precursors that are also HAPs: acrolein from 1,3-butadiene, carbonyl sulfide from carbon disulfide, cresol from toluene, phosgene from chlorinated ethenes. A few, however, are formed from a broad spectrum of VOC precursors. They are formaldehyde, acetaldehyde, propionaldehyde, and methyl ethyl ketone. The approach for modeling these species is discussed later in this section and in Chapter 3.

¹ The later discussion of reactivity in Chapter 5 emphasizes NO₃ concentrations rather than O₃ in characterizing reactivity. When significant concentrations of NO₃ are present, NO₃ is usually a more important nighttime sink than ozone (Ligocki et al., 1991). But NO₃ levels are much more variable and uncertain, so that it is difficult to specify a "typical" annual-average concentration in order to construct a rank order scheme.

TABLE 2-2. Major and minor precursors for secondary HAPs.

HAP	Major Precursors	Minor Precursors
<i>HAPs for which secondary formation may be a major or only source</i>		
acetaldehyde	propene, 2-butene	numerous
acrolein	1,3-butadiene	other 1,3-dienes
carbonyl sulfide	carbon disulfide	
cresol (mainly <i>o</i> -isomer)	toluene	
DDE	DDT	
formaldehyde	ethene, propene	numerous
hydrochloric acid	nitric acid, chlorinated VOC	
methyl ethyl ketone	2-methyl-1-butene, butane, 2-butene, 3-methyl pentane	
N-nitroso-N-methylurea	N-methylurea	
N-nitrosodimethylamine	dimethylamine	trimethylamine
N-nitrosomorpholine	morpholine	
phosgene	tetrachloroethylene, trichloroethylene, vinylidene chloride, methylene chloride	other chlorinated ethenes, ethanes, and methanes
propionaldehyde	1-butene	numerous
<i>HAPs for which secondary formation may be a minor source</i>		
maleic anhydride	toluene, <i>o</i> -xylene	benzene
methanol	2-butene	
methyl isobutyl ketone	2,4-dimethyl-1-pentene	
nitrobenzene	benzene	
4-nitrophenol	phenol, nitrobenzene	
phenol	benzene	
2,4,5-trichlorophenol	2,4,5-T	

A similar reactivity analysis was recently reported (Kelly et al., 1994). Atmospheric lifetimes reported by Kelly et al. are categorized as <1 day, 1–5 days, and >5 days. There are some differences between the reactivity characterizations in Table 2-1 and those of Kelly et al. Kelly et al. used an OH radical concentration of 3×10^6 molecules/cm³ (0.12 ppt) that is more than twice the value used in Table 2-1. For species that are present in both the gas and particulate phases, the lifetimes in Table 2-1 reflect that distribution, whereas those of Kelly et al. are for the gas-phase component only. In other cases, no actual reactivity data exist, and the differences may be due to different estimation techniques.

For a few species, the values presented by Kelly et al. are believed to be incorrect. For example, Kelly et al. reports a 1–5 day residence time for formaldehyde, in contrast to Kao's estimate of 4–10 hours from photolysis and 30–36 hours from reaction with hydroxyl radicals. Howard (1989) also reports a half-life in the sunlit atmosphere of a few hours, and notes that reaction with nitrate radicals may be an important nighttime removal mechanism. Howard further suggests that because of its high solubility, formaldehyde transfers efficiently into rain and surface water, which may be important sinks.

SELECTION OF SPECIES TO BE MODELED

The list of 189 HAPs includes some overlapping entries, and some entries for which no emission data are available. It also includes some entries that are formed in the atmosphere

from precursors that are not on the list. Thus, we made deletions, consolidations, and additions to the list, along with clarifications for ambiguously defined species.

Deletions from the List

Species with No Identified Emissions

Twenty-seven listed HAPs have no reported emissions or emission factors applicable to 1990:

2-acetylaminofluorene	3,3'-dimethyl benzidine	N-nitroso-N-methylurea
4-aminobiphenyl	Dimethyl carbamoyl chloride	N-nitrosodimethylamine
benzidine	1,2-diphenylhydrazine	N-nitrosomorpholine
2-chloroacetophenone	Ethylene imine	phosphine
chlorobenzilate	Hexamethylene-1,6-diisocyanate	1,3-propane sultone
DDE	Hexamethylphosphoramide	propiolactone
diazomethane	Isophorone	toxaphene
1,2-dibromo-3-chloropropane	Mineral fibers	2,4,5-trichlorophenol
dimethyl aminoazobenzene	4-nitrobiphenyl	triethylamine

The reasons for the lack of data differ among these species. Some are no longer produced or used in the United States (e.g., DDE and toxaphene). Thus, current emissions would not be expected, although there is evidence for continued exposure to some of these chemicals, since they are persistent in the environment and may continue to be cycled from other environmental reservoirs (water and soils) to the atmosphere. Modeling of these re-emission mechanisms is beyond the scope of this study. Other HAPs (e.g., diazomethane, mineral fibers) have known uses and very likely have current emissions, but these emissions have not been characterized.

Asbestos

Elevated exposure to asbestos primarily occurs in confined spaces and is often associated with occupational activities. Although there are ambient sources (e.g., mining, construction, and brake wear), emissions are not well characterized. Therefore, asbestos was not modeled.

Caprolactam

This pollutant has been removed from the CAA Section 112(b)(1) list, so it was not modeled.

Radionuclides

Because the nature of radionuclides differs significantly from the other HAPs, they were not modeled.

Phosphorus

Phosphorus exists in three main allotropic forms. White phosphorus is highly toxic and is the pollutant listed as a HAP in Clean Air Act section 112(b). It is used to manufacture phosphoric acid and other phosphorus compounds, smoke screens, tracer bullets, fertilizers,

and gas analysis. It was formerly used in rat and roach poisons and fireworks. White phosphorus does not naturally occur, but can be produced from naturally occurring phosphate rocks. The other forms of phosphorus are less toxic. Black phosphorus resembles graphite and is very stable and insoluble in most solvents. Red phosphorus is used to manufacture phosphor bronzes and metallic phosphides; and as an additive to semiconductors, electroluminescent coatings, safety matches, and fertilizers.

In the preliminary national HAP emission inventory prepared for this study, phosphorus emissions were derived primarily from coal combustion and fugitive dust emissions. Since white phosphorus does not occur naturally, the phosphorus content of dust is unlikely to contain white phosphorus. No information was found regarding the form of phosphorus resulting from coal combustion. Because of the difficulty in identifying emissions of the relevant form of phosphorus, and the likelihood that it constitutes only a small part of the total phosphorus emission inventory, it was omitted from this study.

Titanium tetrachloride

Titanium tetrachloride hydrolyzes in moist air to form TiO_2 and HCl quite rapidly (Miller, 1997). The rapid hydrolysis makes this HAP quite hazardous in a laboratory setting, because it can hydrolyze in the lungs on inhalation. However, its lifetime in ambient air is short enough that it is unlikely to be encountered in any typical exposure situation. Therefore, it was omitted from this study.

Chlorine

Chlorine gas similarly reacts rapidly in the atmosphere, so that it is unlikely to be encountered in any typical exposure situation. Therefore, it was omitted from this study.

Consolidations of Entries

There are four entries on the HAP list for xylene, including the three xylene isomers and an entry for mixed xylenes. There are very few differences between the isomers in terms of emission patterns, reactivity, and health effects. Therefore, we consolidated these entries into a single xylene species. Similarly, there are four entries on the HAP list for cresol. There are some differences in the sources of the individual cresol isomers, since *o*-cresol is formed in the atmosphere to a much larger extent than the other isomers. However, in other respects, including health effects, the three isomers are very similar. We consolidated these entries into a single cresol species.

Additions to the List

Gasoline and Diesel Particulate Matter

Many recent studies (EPA, 1993c, 1994; CARB, 1994) have chosen to characterize potentially toxic emissions from gasoline and diesel engines simply as "gasoline particulate matter" and "diesel particulate matter," rather than identifying specific toxic agents. To facilitate comparison with other studies, gasoline and diesel particulate matter were modeled in this study. Care must be taken in any subsequent analyses not to double-count the impacts of these emissions, since toxic constituents are also tracked.

Formaldehyde Precursors

Modeling studies suggest that roughly 80 percent of ambient formaldehyde in summer and 30 percent in winter is secondary (Ligocki et al., 1991, 1992; Harley and Cass, 1994). Thus, in order to properly characterize formaldehyde concentrations it is important to consider secondary formation. Unfortunately, the processes by which formaldehyde is formed in the atmosphere are complex. Atmospheric reactions of virtually all VOCs will eventually produce some formaldehyde.

Because of the relatively simplistic way that atmospheric reactivity will be addressed in this study, only a fairly simple treatment of formaldehyde precursors is warranted. Two possibilities exist. The first is to consider all VOC as formaldehyde precursors, and use an average conversion rate of VOC to formaldehyde. The disadvantages of this approach are that an appropriate conversion rate is not known, and that all VOC from all sources would incorrectly be assumed to produce formaldehyde with equal efficiency. The second possibility, the approach we adopted, is to weight the precursors according to their formaldehyde yield. We added a single formaldehyde precursor species. Emissions of major formaldehyde precursors were weighted and assigned to this species during emissions processing (see Chapter 3).

Acetaldehyde Precursors

Modeling studies suggest that roughly 90 percent of ambient acetaldehyde in summer and 40 percent in winter is secondary (Ligocki et al., 1992). As with formaldehyde, a wide variety of VOCs produce acetaldehyde. We added a single acetaldehyde precursor species. Emissions of major acetaldehyde precursors were weighted and assigned to this species during emissions processing (see Chapter 3).

Propionaldehyde Precursors

The relative importance of primary emissions and secondary formation of propionaldehyde is not known. However, by analogy to the other aldehydes, secondary formation should not be overlooked. Less information is available in the literature on precursors for propionaldehyde, but the major precursors are expected to be olefins with a double bond in the 3-position. We added a single propionaldehyde precursor to the list.

Acrolein Precursors

1,3-Butadiene is the only precursor for acrolein that is emitted in any significant quantities to the atmosphere. Since 1,3-butadiene is already on the HAP list, there is no need for an additional acrolein precursor species.

Methyl Ethyl Ketone (MEK) Precursors

The relative importance of primary emissions and secondary formation of MEK is not known. MEK is used as a solvent, and primary emissions may be large. Existing atmospheric chemical mechanisms include numerous pathways for the formation of MEK, but because these are condensed mechanisms, MEK is used as a surrogate for numerous related chemical species. A single MEK precursor species was added.

Phosgene Precursors

Phosgene, the chlorinated analog to formaldehyde, is produced in reactions of chlorinated terminal olefins. It is also produced in the reactions of chlorinated methanes and ethanes. Many of the expected atmospheric precursors to phosgene are on the HAP list. They are:

- chloroform (trichloromethane)
- carbon tetrachloride (tetrachloromethane)
- methylene chloride (dichloromethane)
- ethylidene dichloride (1,1-dichloroethane)
- hexachlorobutadiene
- hexachloroethane
- trichloroethylene
- tetrachloroethylene
- vinylidene chloride (1,1-dichloroethene)

Based on the reaction rates and estimated atmospheric abundance of each of the phosgene precursors, Grosjean (1991a) estimated that tetrachloroethylene, trichloroethylene, vinylidene chloride, and methyl chloride would be the predominant precursors for phosgene in the atmosphere. Since these species are already on the HAP list, there is no need for an additional phosgene precursor species.

Cresol Precursors

Toluene is the only known precursor for cresol in the atmosphere. Since toluene is already on the HAP list, there is no need for an additional cresol precursor species.

Dimethyl Sulfate and Diethyl Sulfate Precursors

Some evidence suggests that dimethyl sulfate is present in ambient air (Eatough et al., 1986), and it has been suggested that it may be produced in atmospheric reactions of sulfuric acid with methanol. Diethyl sulfate has not been measured in ambient air, but could conceivably be produced in an analogous reaction with ethanol. However, other researchers have been unable to duplicate these findings or identify a specific mechanism for the reaction (Japar et al., 1990a,b). Therefore, secondary formation of these species will not be considered.

N-Nitroso Compound Precursors

These compounds may be produced in the atmosphere (Grosjean, 1991c). However, emissions of their expected precursors and product yields are not well known. Thus, these species were not modeled in the ambient portion of this study.

Hydrochloric Acid Precursors

Hydrochloric acid (HCl) is produced in the atmospheric reaction of sea salt (NaCl) with nitric acid (Pilinis and Seinfeld, 1987). Nitric acid, in turn, is produced by the atmospheric oxidation of nitrogen oxide (NO_x) emissions. Because neither sea salt nor NO_x were modeled in this study, this formation pathway for HCl was not included.

Other Clarifications

Naphthalene and Polycyclic Organic Matter (POM)

The definition of POM presented in the CAA specifically includes naphthalene. However, since naphthalene is a separate entry on the list, it was modeled separately to avoid double-counting. Alkyl naphthalenes were included in POM.

Lead Compounds

Elemental lead is specifically excluded from the HAP list since it is covered under regulations for lead as a criteria pollutant. However, because the form of lead emissions is not specified in the emission databases available, all lead compounds were modeled for this study.

Arsenic Compounds and Other Metals

The definition of "arsenic compounds" includes both particulate-phase arsenic and gaseous arsine. Other metals (e.g., antimony) may also have gas and particle components. However, for this study, only the dominant particulate-phase emissions were modeled for all metals except mercury.

Dioxins and Furans

Only 2,3,7,8-tetrachlorodibenzodioxin and "dibenzofurans" are included on the HAP list. However, for this study, all chlorinated dioxin and furan congeners will be modeled as a single species using the toxic equivalence approach, in which dioxin and furan congeners are weighted according to their toxicity. The toxicity equivalence factors (TEFs) are listed in Table 2-3.

TABLE 2-3. Toxicity equivalence factors (TEF) for chlorinated dibenzodioxins (CDDs) and chlorinated dibenzofurans (CDFs). (Source: EPA, 1989b)

Compound	TEF	Compound	TEF
Mono-, Di-, and Tri-CDDs	0	Mono-, Di-, and Tri-CDFs	0
2,3,7,8-TCDD	1	2,3,7,8-TCDF	0.1
Other TCDDs	0	Other TCDFs	0
2,3,7,8-PeCDD	0.5	1,2,3,7,8-PeCDF	0.05
Other PeCDDs	0	2,3,4,7,8-PeCDF	0.5
2,3,7,8-HxCDD	0.1	Other PeCDFs	0
Other HxCDDs	0	2,3,7,8-HxCDF	0.1
2,3,7,8-HpCDD	0.01	Other HxCDFs	0
Other HpCDDs	0	2,3,7,8-HpCDF	0.01
OCDD	0.001	Other HpCDFs	0
		OCDF	0.001

Coke Oven Emissions

Many of the listed HAPs are present in coke oven emissions; however, because the aggregated emissions are the basis for some health studies these emissions, and they are a separately listed HAP, they were also tracked as a group. As with gasoline and diesel particulate matter, care must be taken in subsequent analyses not to double-count the impacts of these emissions.

Final List of HAPs To Be Modeled

After deleting 33 HAPs for the reasons discussed above, and consolidating cresols, xylenes, and dioxin/furans into single species, the final list of HAPs to be modeled contains 148 listed HAPs, as well as coke oven emissions. Four HAP precursor species and gasoline and diesel particulate matter were also modeled. We also modeled carbon monoxide (CO), which has been used as a surrogate for toxics from motor vehicles (EPA, 1993c). Modeling CO in this study has several benefits. First, it allows for model performance evaluation using the extensive nationwide monitoring database for CO. Second, it allows for an assessment of the use of CO as a surrogate for toxics, and could provide scaling factors between toxic and CO exposures that could be used in future assessments for which extensive toxics modeling may not be feasible.

3 HAP EMISSION INVENTORY DEVELOPMENT

This chapter describes the preparation of a nationwide emission inventory for the toxic species and precursors identified in Chapter 2 for the 1990 base year. It begins with a discussion of the data sources used and the processing steps needed to prepare the inventory for input into the exposure model. Toxic profiles by source category are reviewed, the approach for processing emissions of toxic precursors is outlined, and uncertainties are assessed. The results of the emission inventory processing are presented in Chapter 4.

EMISSION INVENTORY DEVELOPMENT METHODS

The data sources available for the estimation of HAP emissions fall into three categories: HAP inventories, HAP emission factor databases, and HAP profile databases. HAP inventories include the Toxic Release Inventory (TRI; compiled from direct self-reports by individual large stationary facilities) (EPA, 1991b), local HAP inventories, and national inventories for selected HAPs such as mercury (EPA, 1995a). The main HAP emission factor databases are the EPA Factor Information and Retrieval System (FIRE), and the AP-42 database. Speciation databases include the EPA SPECIATE database (EPA, 1992a) and the California Air Resources Board speciation database (CARB, 1991a, 1991b). Speciation profiles are also available from the technical literature, generally developed to support receptor modeling analyses (e.g., Scheff et al., 1989; Harley et al., 1992).

There are thus three potential approaches for deriving nationwide toxic emissions; Figure 3-1 shows the processing steps associated with each. To use HAP inventories, such as TRI, as the starting point, the only processing needed is spatial and temporal allocation of emissions. This approach may be characterized as "direct" and "bottom-up," since HAP emissions are reported directly, rather than being inferred from other information, and the inventory is built up from individual facilities.

EPA has prepared national "interim inventories" of 1990 county-level emissions for VOCs and PM₁₀ (EPA, 1993a; Pechan, 1994) which are suitable for development of speciated HAP emissions estimates. These inventories contain emissions from point sources, area sources, nonroad mobile sources, and onroad motor vehicles. The speciation method of estimating HAP emissions uses two kinds of data in combination: first, emissions estimates for volatile organic compounds (VOCs) and particulate matter (PM₁₀); and second, a set of speciation profiles which allow derivation of HAP emissions estimates from VOC and PM₁₀ emissions estimates. This method makes use of the fact that many gaseous HAPs are constituents of VOC emissions, and many particle-phase HAPs are constituents of PM₁₀ emissions. Speciation profiles provide source category-specific estimates of the presence of specific pollutants in the VOC and PM₁₀ emissions from facilities in each source category. For example, a speciation profile for VOC emissions from refineries would indicate the presence of benzene, toluene, and other organic chemicals as a percentage of total refinery VOC emissions. Emissions of specific organic pollutants from any refinery can then be estimated by multiplying the refinery's total VOC emissions by the appropriate speciation profile percentage for each pollutant. Emissions estimates for gaseous HAPs may be derived by

speciation of VOC emissions data, while emissions for particulate HAPs may be derived by speciation of PM_{10} emissions data. This approach may be characterized as “indirect” and partially “top-down,” since HAP emissions are inferred from VOC or PM_{10} emissions, and for some source categories, such as area sources, national emission estimates are allocated to counties and source categories based on indicators such as population and employment. Point source emissions in the EPA National 1990 VOC and PM_{10} inventories, on the other hand, are facility-specific (“bottom-up”) but are generally inferred from activity data, such as fuel use.

Finally, HAP emission factors may be used. Emission factors specify the magnitude of emissions released for various types of activities. For example, an emission factor might specify the amount of benzene emitted for each gallon of fuel oil burned in an electric power plant. Therefore, to use HAP emission factors as the starting point, a national inventory of activity (usage) by source category is needed. This approach may be characterized as “indirect” and “bottom-up,” since HAP emissions are inferred from activity levels reported for individual facilities or counties.

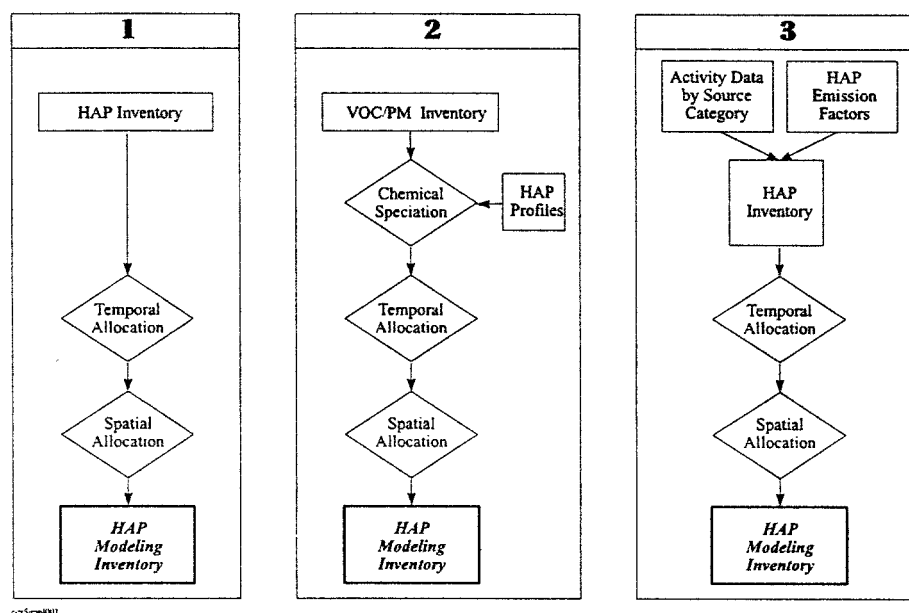


FIGURE 3-1. Approaches to processing emission data from different sources.

Each of these approaches was considered for use in this study. Building up a toxic inventory through the use of toxic emission factors combined with activity levels (method 3) was rejected because the necessary activity information is not available for all source categories nationwide, and because this approach would be too resource-intensive to be feasible for the present study. Direct use of the TRI inventory (approach 1) does not address area and mobile emissions, which are important sources of toxic emissions, or many types of point sources. Local HAP inventories do not provide national coverage, and those that are available may not cover a consistent time period.

Comprehensive national inventories are available for only a few species. An exception is the National Toxics Inventory (Version 9702) recently developed by the EPA's Emission Factors and Inventory Group (EFIG), which includes emissions of 214 HAPs resolved by

county. The inventory is being constructed using the 1993 TRI inventory, some city-specific inventories, and some special studies (method 1), speciated national VOC and PM₁₀ inventories for mobile sources (method 2), and emission factors combined with activity estimates for the remaining sources (method 3). It is anticipated that as additional source-specific data are compiled by TRI or in state and local inventories, these data will be added to the inventory, replacing estimates made with method 3.

Top-down and bottom-up inventory approaches both have strengths and weaknesses. With a bottom-up approach, whether direct or indirect, emphasis is placed on accurate emission estimates for individual facilities. Thus, the primary advantage of a bottom-up approach is that the resulting data for any particular source are likely to be more accurate than a top-down estimate. The primary disadvantage is the large resource requirement to obtain comprehensive coverage of all relevant sources. In the indirect bottom-up approach, source categories with unknown emission factors are omitted.

With a top-down approach the emphasis is on comprehensive accounting of all emissions, and detailed assignment of emissions to source categories is of secondary importance. Emissions from source categories with unknown emission factors and/or speciation profiles are estimated based on similar source categories. This inevitably involves a subjective assessment and introduces some uncertainty into the process. However, it is necessary in order to have any hope of achieving adequate model performance for a modeling study, such as this. In addition to lower resource requirements, another advantage of the top-down approach is consistent treatment nationally. If local inventories are mixed into a national inventory, identical facilities located in different regions of the country might have totally different reported emissions, due to differences in emission estimating techniques. In the top-down approach a consistent methodology is used throughout. This feature was considered important to the geographic comparisons that are among the major objectives of this study.

Thus, the basic approach adopted for this study is to combine nationwide county-level VOC and PM₁₀ emissions with speciation profiles for each source category (approach 2). This approach takes advantage of recently developed national inventories for VOCs and PM₁₀ (EPA, 1993a; Pechan, 1994) and existing emission processing software used to chemically speciate VOC emissions for input into photochemical models.

A previous modeling study (UAM-Tox) (Ligocki et al., 1992) noted that this approach for deriving HAP emissions from a VOC inventory can occasionally result in erroneous emission estimates. These errors can be large enough to have a major impact on model results. For example, an error in the formaldehyde content of the profile for catalytic cracking resulted in modeled formaldehyde concentrations in Houston that were overpredicted by a factor of 50. An error in the profile for "gasoline marketed" led to the unlikely result that gasoline evaporation was the largest source of POM (mainly naphthalene) in urban inventories. That study produced a set of updated profiles and profile-source category assignments that reduced some of these types of errors. However, there are some inherent limitations to the national VOC inventory that preclude accurate HAP speciation. In particular, some chemical manufacturing processes have VOC emissions listed under general source categories ("miscellaneous chemical production") that provide no information on what is being produced. Without that information, accurate identification of HAP emissions is impossible.

In recognition of this limitation in the VOC inventory, an alternative approach was adopted for major manufacturing sources that relies on the air emissions data reported in the Toxic Release Inventory. The assumption was that the self-reported information in the TRI would more accurately portray the chemical *identity* of emissions from major manufacturing facilities. However, this approach has limitations as well because the *quantitative* emission estimates in the TRI are highly uncertain. Some comparisons of the two approaches and assessment of uncertainty in the TRI emissions are presented in Attachment 1.

NATIONWIDE EMISSION DATA SOURCES

Toxic Release Inventory

Emissions of HAPs from major industrial sources are available from the Toxic Release Inventory (TRI), an annual compilation of information on the release of over 300 chemicals and chemical groups by manufacturing facilities (EPA, 1991b). Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 requires that facilities report this information to the EPA and that the EPA report it to the public. The reporting requirement applies to owners and operators of facilities that have 10 or more full-time employees, that are in Standard Industrial Classification (SIC) codes 20 through 39, and that manufacture, import, process, or otherwise use a listed toxic chemical in excess of specified threshold quantities. These are processing of more than 25,000 pounds per year or otherwise using more than 10,000 pounds per year of a listed HAP. The database includes location and other site-specific information about each facility as well as quantity of each chemical released annually into different environmental media or transferred off site.

Refineries. Refineries are among the source categories required to report emissions estimates to TRI. As discussed in Attachment 1, TRI emission estimates for refineries appear to be both inaccurate and incomplete in terms of the number of species included. Although the quality of the VOC emission data for refineries in the 1990 national VOC inventory has not been investigated and may also be uncertain, the general approach of using activity levels and emission factors that was used for the development of the national VOC inventory is likely to result in more accurate emission estimates than available from the TRI. Therefore, refineries were separated from other manufacturing sources and processed using the speciation approach.

Facility Locations. The TRI database contains two sets of location parameters for each facility: one reported by the facility and one specified by the EPA, which is associated with the zip code reported by the facility. The second set of location parameters was added by the EPA because a high percentage of the self-reported location parameters were erroneous. For example, in one sample area of 54 census tracts, we determined that approximately 25 percent of the self-reported location parameters place the facility in the wrong county. However, because zip code areas tend to be larger than census tracts in urban areas, the zip code centroid may be in a different census tract than the facility. Therefore, we used the self-reported locations for data that passed a screening test as follows: (1) the specified location is in the specified county of the facility, and (2) the specified location is within a reasonable distance of the specified zip code centroid, characterized according to the average size of zip code areas within the vicinity of the source. For locations that did not pass the

screening test, we supplemented the TRI location information with an EPA database of enhanced facility locations (Hall, 1996).

National 1990 VOC and PM₁₀ Inventories

The 1990 EPA National Interim Inventory (EPA, 1993a) contains county-level emissions for VOC, carbon monoxide (CO), and nitrogen oxides (NO_x) for the contiguous 48 states. It contains emissions from point sources, area sources, nonroad mobile sources, and onroad motor vehicles. This inventory was developed for use in the EPA's Regional Oxidant Model (ROM), which is used to provide boundary conditions for urban-scale photochemical models. It is referred to by the EPA as an "interim" inventory because it does not include emission data developed by individual states as part of their State Implementation Plans (SIPs). The intent was to integrate the SIP data into the national inventory as they became available. Although this process has begun, the version of the VOC inventory used for this study does not incorporate any SIP emission data.

The definition of point and area sources in these inventories differs from that used to define reporting requirements for the TRI inventory: processing more than 25,000 pounds or otherwise using more than 10,000 pounds of a listed HAP. For the National 1990 VOC and PM₁₀ Inventories any source that emits more than 100 tons per year of a criteria pollutant (VOC, CO, NO_x, SO₂, or PM₁₀) is considered a point source; otherwise it is considered an area source.

A starting point for portions of the 1990 national inventory was the 1985 National Acid Precipitation Assessment Program (NAPAP) inventory. The NAPAP inventory was developed for use with the Regional Acid Deposition Model (RADM) and focused on emissions of acid deposition precursors (SO₂ and NO_x). The 1990 inventory incorporates newer data for fossil-fuel steam utilities, solvent usage, and onroad and nonroad mobile sources. Updated emission factors were used for several source categories. In addition, point source emissions were adjusted to reflect an assumed 80 percent rule effectiveness for control efficiencies.

For point sources, each data record in the inventory potentially contains information on the source category, location (coordinates), facility and stack identifiers, operating schedule, control efficiencies, and stack parameters (height, temperature, and flow rate) in addition to reporting annual-average emissions for VOC, NO_x, and CO. Not all of this information is provided for all sources, however.

The electric utility data are based on boiler-level data submitted to the U.S. Department of Energy (DOE) Energy Information Administration, and include data for facilities with boilers of 10 megawatt or greater capacity. The nonutility point source emissions data in the National Inventory were projected to 1990 by industry class from the information contained in the 1985 NAPAP inventory, which included all point sources emitting more than 100 tons per year of any of the criteria pollutants: NO_x, SO₂, VOC, TSP, or CO. Thus, new nonutility facilities built between 1985 and 1990 are not included in the 1990 inventory. However, because the growth of total emissions by industry class was estimated, the emissions from new nonutility facilities would be included, but allocated to existing facilities. This may introduce significant uncertainties in the outdoor HAP concentration estimates for tracts dominated by new nonutility combustion point sources built between 1985 and 1990. Assuming for most industry classes that only a small fraction of 1990 emissions come from facilities built between 1985 and 1990, the misallocation of those

emissions to older facilities would introduce only a correspondingly small bias toward overestimation in the older facilities, which is likely to be small compared to the uncertainty in the emissions growth estimate itself.

The area source inventory includes emissions from sources smaller than the point source emission-level cutoff, and is reported as county-level emission totals by source category. For area sources, each data record in the inventory includes state and county codes, area source category code, and annual emissions. Area source solvent emissions in the 1990 inventory were obtained using a mass balance on solvent consumption and removal. National solvent consumption data were obtained from the U.S. Paint Industry database and from industrial solvent marketing reports. The emission estimates for solvent usage were calculated at the national level, and disaggregated to the county level based on population (consumer categories) and employment data (industrial categories). Solvents associated with pesticides were allocated to counties according to farm acreage. Area source emissions from most other source categories were obtained from the 1985 NAPAP inventory and projected to 1990 using economic indicators. Revised emission estimates were also obtained for refinery fugitive emissions, hazardous waste treatment, storage, and disposal facilities, residential wood combustion, and gasoline marketing. The assumption of 80 percent rule effectiveness was applied to controlled sources.

The mobile source inventory includes MOBILE5 emission factors for onroad sources and the 1991 EPA Nonroad Engine study (EPA, 1991a) for nonroad sources. Onroad mobile emissions are provided at the county level as a function of vehicle class and roadway type. MOBILE5 requires information on speed, gasoline volatility (RVP), and temperature to calculate emission factors. The 1990 inventory includes average speeds developed on a national level as a function of vehicle class and roadway type. Minimum and maximum temperatures and average RVP were developed by season for each state. Estimates of vehicle miles traveled (VMT) by roadway type were obtained from the Highway Performance Monitoring System. These data are reported for rural, small urban, and large urban areas. They were converted to a county basis, and allocated to vehicle classes. Onroad mobile emissions for 1990 are available as annual averages or by season.

The 1990 national VOC inventory, 1993 version (EPA, 1993a), was used in this study to derive emission estimates for volatile HAPs and some semivolatile HAPs such as POM. The June 1995 version of the national PM_{10} inventory (Pechan, 1994) was used in the present study to derive emissions for metals and dioxin. The national PM_{10} inventory was developed according to a methodology similar to that used in the development of the VOC inventory, but also utilized some additional data sources, including some incorporation of SIP data as well as data from a recent inventory developed for the Grand Canyon Visibility Transport Commission. The PM_{10} inventory utilized the PART5 (EPA, 1995c) model for onroad mobile sources.

Evaluation of paved road dust estimates in the national PM_{10} inventory revealed total $PM_{2.5}$ values more than twice as high as those for diesel exhaust. However, tunnel PM_{10} composition data (NEA, 1987) and ambient $PM_{2.5}$ composition data for the Los Angeles area show that road dust accounts for a much smaller fraction of $PM_{2.5}$ concentrations than diesel exhaust. Further, the tunnel study and numerous ambient $PM_{2.5}$ and PM_{10} studies (e.g., Gray, 1986; Solomon et al., 1989; Ligocki et al., 1993b) found that coarse road dust concentrations greatly exceeded fine concentrations, in contradiction to the values estimated in the national PM_{10} inventory. Based on these findings, we believe the inventory PM_{10}

emissions for paved road dust may be high and the fine fraction of paved road dust may be greatly overstated. For that reason, road dust emissions were omitted from the national HAP inventory. Unpaved road dust contains some chromium and generally small amounts of manganese, nickel, arsenic, selenium, and cadmium. Omitting these sources may result in underestimates of concentrations of these HAPs and exposures.

Recent National VOC and PM₁₀ Emission Inventory Revisions. The 1990 national interim inventory (Int90), 1993 version (EPA, 1993a), was used in this study to derive emission estimates for gaseous HAPs; and the 1995 version (Pechan, 1994) was used to derive emissions for particulate HAPs. The 1990 National Emission Trends (NET) Inventory developed by EPA was made available in May 1997. This inventory was developed to serve as a composite inventory for use in both the EPA National Trends Report, and for modeling and control strategy analyses. Included in the NET90 inventory are data collected as part of the Ozone Transport and Assessment Group (OTAG), the Grand Canyon Visibility Transport Commission (GCVTC), the EPA Interim Inventory, and the EPA National Particulate Inventory (NPI). In addition, new information on emission factors for utilities from EPA's Acid Rain Division are included. Comparisons for VOC and PM₁₀ emissions between the national interim inventory and the NET inventory for the 48 contiguous United States and the District of Columbia are presented in Table 3-1 by source type: point, area, onroad mobile, and nonroad mobile. Area sources are further disaggregated into dust and non-dust categories for PM₁₀. The area source dust category includes emissions from paved/unpaved roads, wind erosion (construction, geogenic), agriculture production (live stock, crops tilling), building/road construction and unpaved airstrip. Differences in VOC and PM₁₀ emissions between the inventories used for this study and the more recent ones, described below, are only rough guides to implied differences in emissions of HAPs, since the speciation profiles applied to these emissions vary widely.

VOC Emissions Comparisons. Area sources are the largest contributors to VOC emissions in the inventories (44 percent in the Int90 and 39 percent in the NET90), followed by onroad mobile source (29 percent in the Int90 and 35 percent in the NET90), point source (18 percent in the Int90 and 15 percent in the NET90), and nonroad mobile source (9 percent in the Int90 and 11 percent in the NET90). The VOC emissions from the Int90 are 33 percent higher than the NET90 overall. The most significant differences between the inventories are from point and area sources. VOC emissions from point source in the Int90 are 68 percent higher than the NET90, and emissions from area source in the Int90 are 51 percent higher than the NET90.

There are approximately 2400 Source Classification Codes (SCCs) used in the inventories to estimate point source emissions by process. The VOC emissions are higher in the Int90 than the NET90 for 729 SCCs, with emission differences 2,682,459 tons/year; and VOC emissions are lower in the Int90 for 1,660 SCCs, with emission differences 930,673 tons/year. The overall point source VOC emission difference between the inventories is 1,751,786 tons/year.

For point sources, there are four SCCs with the VOC emission differences between the inventories more than 90,000 tons/year. Because the CEP inventory used TRI estimates for manufacturing point sources, not all emissions from these four SCCs were used in the CEP inventory. The SCCs are: chemical manufacturing miscellaneous, not classified (272,454 tons/year higher in the Int90, less than 1% used in the CEP inventory); chemical manufacturing miscellaneous, waste gas flares (155,401 tons/year higher in the Int90);

organic chemical storage, pressure tanks, 1,3-butadiene (102,806 tons/year higher in the Int90, not used in the CEP inventory); and external combustion boiler, industrial, natural gas (91,262 tons/year higher in the Int90).

The VOC emissions from area sources in the Int90 are 50 percent higher than the NET90. A more detailed source category disaggregation is presented in Table 3-2. The most significant changes for area sources between the inventories are emissions from waste disposal, treatment and recovery; and solvent utilization. The subcategories for these two categories are also shown in Table 3-2. Among the subcategories for waste disposal, treatment and recovery, the biggest changes are emissions from TSDFs and open burning. Since HAP emissions from TSDFs were available from EPA (Coburn, 1995), the Int90 VOC emission estimates for this category were not used in the CEP inventory. In the subcategories for solvent utilization, the biggest changes are emissions from consumer solvent utilization, industrial adhesives, and degreasing.

Another estimate of VOC emissions from consumer solvents is available from the results of a survey sponsored by EPA's Emission Standards Division (ESD; presented in EPA, 1995g). The survey targeted manufacturers and distributors of consumer products to determine product sales, VOC content, and HAP formulation. The national Interim VOC Emissions Inventory estimates for this category were based on solvent usage rates obtained from 1989 industrial marketing reports. A comparison of VOC emissions from consumer solvents among the Int90 inventory, the NET90 inventory, and the ESD survey is presented in Table 3-3. Although the NET90 inventory has more subcategories than the ESD survey, the overall total of the NET90 inventory matches the ESD survey well. In contrast, the Int90 inventory total is almost 70 percent higher than the ESD survey.

PM₁₀ Emission Comparisons. PM₁₀ emissions are dominated by the area dust category in the inventories, with 92 percent in the Int90 and 85 percent in the NET90. The area dust category is also the one with the largest discrepancy between the inventories (53 percent higher in the Int90 than in the NET90). The PM₁₀ emissions from point, non-dust area, and nonroad mobile sources are lower in the Int90 than the NET90, with Int90 to NET90 ratios 0.68, 0.73 and 0.87, respectively; and emissions from onroad mobile source are 6 percent higher in the Int90 than the NET90.

PM₁₀ emissions from dust area sources are further disaggregated in Table 3-4. Dust area sources are dominated by emissions from unpaved roads (32 percent in the Int90 and 45 percent in the NET90). The biggest changes of PM₁₀ emissions between the inventories are from paved roads, wind erosion, and crops tilling. Based on the findings discussed in detail in Chapter 4, we believe that the Int90 PM₁₀ emissions for paved road dust are high and the fine fraction of paved road dust may be greatly overstated. Therefore, most dust categories of PM₁₀ emissions were not used in the CEP inventory; that is, emissions from paved and unpaved roads, wind erosion, and crop tilling were omitted. Only 1.7 percent of PM₁₀ emissions from dust area sources in the Int90 were used in the CEP inventory.

Speciation Data

Emissions of HAPs were derived from VOC and PM₁₀ emissions by application of speciation profiles for each source type. The SPECIATE database (EPA, 1992a) contains VOC and PM₁₀ weight percent profiles for many source categories. This database was compiled from data from a variety of sources, including both source tests and estimates. Each profile

contains a data quality code ranging from A to E; profiles with D and E ratings have very high uncertainties.

Previous studies have noted problems with specific profiles in the SPECIATE database (Ligocki et al., 1992; Harley et al., 1992; Korc and Chinkin, 1993). Some of these errors were identified and the profiles modified during the UAM-Tox photochemical modeling study previously conducted by SAI for the EPA (Ligocki et al., 1992). In that study numerous profiles were also modified by incorporating HAP data obtained from the EPA "Locating and Estimating" documents for five HAPs (benzene, butadiene, formaldehyde, acetaldehyde, and POM). Therefore, the starting point for development of the HAP inventory was the set of profiles in SPECIATE version 1.5, supplemented by profiles modified in the UAM-Tox study.

These were supplemented by additional profiles from the recent update to AP-42 (EPA, 1993b), from profiles developed by the California Air Resources Board (CARB, 1991), source category-specific studies by EPA (1989, 1993c, 1993e, 1994, 1995b), HAP-specific studies by EPA (1994, 1995a), and from the literature (Battye and Williams, 1994; Burnet et al., 1990; Edgerton et al., 1985; Hare and White, 1991; Harley et al., 1992; Harley and Cass, 1994; Ingalls, 1991; Lipari et al., 1984; Miller et al., 1994; Sagebiel et al., 1996; Scheff et al., 1992; Volkswagen 1989; Ward and Hao, 1992; Ward et al., 1993; Warner-Selph, 1993, 1989; Hildemann et al., 1991; and Scheff et al., 1994). In some specific cases, toxic emission factors from FIRE were combined with VOC or PM₁₀ emission factors from AP-42 to create mass fractions that were subsequently inserted into the appropriate profiles. The review and development of HAP profiles are discussed in Attachment 3.

Municipal Waste Combustor Database

A national inventory of municipal waste combustor (MWC) locations and emissions was developed by SAI for use in a HAP deposition modeling study (Guthrie et al., 1995). Analyses of MWC emissions in the national PM₁₀ inventory showed that many MWC facilities active in 1990 are missing from the inventory. Some facilities are missing because they were constructed after 1985, and thus were not in the NAPAP inventory from which the 1990 inventory was derived. Others are too small to be considered point sources. However, for a significant number of facilities, there was no obvious reason for their omission from the inventory. It may be that MWC were not a high-priority source category in the NAPAP inventory because their SO₂ emissions are relatively low. Because this alternative inventory was available, it was used as a starting point for the present study. The inventory was expanded to include the larger number of target HAPs of interest in the Cumulative Exposure study and facility-specific data for additional facilities. It was also modified to reflect actual rather than permitted emissions.

Hazardous Waste Treatment, Storage, and Disposal Facility Database

An inventory of Hazardous Waste Treatment, Storage, and Disposal Facility (TSDF) locations and HAP emissions was obtained from the EPA (Coburn, 1995). This inventory was based on survey data from 1986 for all permitted offsite facilities, and was updated to approximate 1991 emissions. Process information and HAP physical/chemical properties were used to estimate emissions of HAPs from over 400 facilities, out of approximately 3,800 TSDF facilities, across the country (EPA, 1995d). These estimates were originally

used by the EPA to obtain a national estimate of total HAP emissions, and the uncertainty in the estimates is much larger for individual HAPs and facilities. However, despite the uncertainties, this inventory was judged to be superior to the alternative, which would be the application of a single HAP profile to all TSDf VOC emissions from all facilities.

In addition to these facility-specific data, we intended to develop an average TSDf profile based on the information provided by the EPA and use it in conjunction with TSDf VOC emission estimates from the 1990 National VOC Inventory for the TSDfs not included in the EPA survey. However, evaluation of the data revealed serious concerns about the quality of the national VOC emission data for TSDfs. Thus, TSDfs that were not included in the EPA survey are omitted from the inventory.

National Herbicide Use Database

Some of the listed HAPs are pesticides or herbicides, and emissions from their application would not be captured using the approach and databases described above. An alternative data source for application of pesticides and herbicides is the National Herbicide Use Database, produced by the National Center for Food and Agriculture Policy (NCFAP) in Washington, DC. It contains data on herbicide, fungicide, and insecticide use in agricultural crop production throughout the contiguous United States. Estimates of use for 96 active ingredients on 84 crops are included. Data available for each crop include 1987 estimates for the number of acres of harvested crop, the average rate of use per acre, the total number of acres treated, and the total pounds of active ingredient used. This information can be aggregated on a county, regional, state, or national level. Crop acreage estimates were taken from the 1987 Census of Agriculture, and estimates of chemical use were taken from publicly available federal and state government reports. This information was aggregated into summary statistics by the NCFAP, based on surveys conducted by the Cooperative Extension Service of the U.S. Department of Agriculture and information obtained from manufacturers.

Developing emission estimates from the usage data requires information on rates of loss of these species due to spray drift and/or volatilization from surfaces. The fraction of applied pesticide that is lost through these mechanisms is a complex function of physical/chemical properties of the chemical, mode of application, meteorological conditions, and soil and crop characteristics. Because accurate estimation of these parameters nationwide would be a formidable task, a screening analysis was performed to determine whether HAP emissions from agricultural pesticide application would lead to nonoccupational inhalation exposures that were significant by comparison to ingestion exposures. This analysis, provided as Attachment 2 to this report, showed that inhalation exposures were not likely to be important. Therefore, no further processing of the pesticide application data was performed.

SOURCE CATEGORY SUMMARY

In summary, the following data sources were used in this study:

- The 1990 National VOC and PM₁₀ Inventories combined with HAP speciation profiles from a variety of sources
- The 1990 Toxic Release Inventory
- An inventory of MWC locations and emissions

- An inventory of TSDF locations and HAP emissions.

The definition of source categories to be used for this study was dictated by the data sources. As described in Attachment 1, refineries were removed from the TRI-derived manufacturing point source category because of concerns regarding the accuracy of quantitative emission estimates for refineries in the TRI and because an alternative approach was available. Refineries were retained as a separate category and emissions were derived from the National VOC and PM₁₀ inventories in conjunction with available speciation profiles. Similarly, the TRI does not include emissions associated with combustion sources at manufacturing facilities. Since most metal production involves the use of furnaces, ovens, etc., we assumed that these emissions would not be accurately represented in the TRI. Therefore, these emissions were derived from the National VOC and PM₁₀ inventories as part of "other point source" category.

Finally, the area source category was split into manufacturing and nonmanufacturing subcategories at the EPA's request. Area manufacturing sources are mainly comprised of the following activities: chemical manufacturing, food and kindred products, secondary metal production, petroleum refining, wood products, rubber and plastics, industrial surface coating, degreasing, miscellaneous industrial solvent utilization, and industrial adhesive application. Area non-manufacturing sources are mainly comprised of: fuel combustion, oil and gas production, construction, non-industrial surface coating (architectural coating, auto refinishing, traffic markings and other special purpose coatings), dry cleaning, commercial and consumer solvent utilization, gasoline service stations, on-site incineration, open burning, and wastewater treatment.

The final source categories and their data sources are:

- Metal manufacturing point sources (excluding combustion sources)—obtained from the TRI.
- Non-metal manufacturing point sources (excluding refineries and combustion sources)—obtained from the TRI.
- Municipal waste combustors—obtained from separate MWC inventory using speciation profiles described in Attachment 3.
- TSDFs—obtained from separate TSDF HAP inventory.
- Refineries—obtained from the VOC and PM₁₀ inventories using speciation profiles described in Attachment 3.
- Other point sources (excludes MWC and TSDFs, includes manufacturing combustion sources) —obtained from the VOC and PM₁₀ inventories using speciation profiles described in Attachment 3.
- Area manufacturing sources—obtained from the VOC and PM₁₀ inventories using speciation profiles described in Attachment 3.
- Area non-manufacturing sources (excludes TSDFs) —obtained from the VOC and PM₁₀ inventories using speciation profiles described in Attachment 3.
- Onroad mobile sources—obtained from the VOC and PM₁₀ inventories using speciation profiles described in Attachment 3.

- Nonroad mobile sources—obtained from the VOC and PM₁₀ inventories using speciation profiles described later in Attachment 3.

Allocation of Emissions Among Point and Area Sources

The allocation of emissions among point and area sources in the CEP inventory is not consistent with the area source definition specified by Title I, Section 112(a) of the CAA. According to that definition a "major source" is any stationary source (including all emission points and units located within a contiguous area and under common control) of air pollution that has the potential to emit, considering controls, 10 tons or more per year of any HAP or 25 tons or more per year of any combination of HAPs. An "area source" is any stationary source of HAPs which does not qualify as a major source. Point sources in the CEP inventory include all facilities reporting to the TRI, and facilities classified as point sources in the national Interim VOC or PM₁₀ Inventories. The TRI requires reporting from any facilities processing more than 25,000 pounds (12.5 tons) or otherwise using more than 10,000 pounds (5 tons) annually of a listed HAP. Thus, some of the facilities reporting to the TRI may not qualify as "major sources" under the Section 112 definition. For the national 1990 VOC and PM₁₀ Inventories any source that emits more than 100 tons per year of a criteria pollutant (VOC, CO, NO_x, SO₂, or PM₁₀) is considered a point source. Because only a fraction of the VOC and/or PM₁₀ emitted is composed of HAPs, some of these sources may not be considered "major sources" according to the Section 112 definition. Moreover, it is also possible for a facility to emit more than 10 tons of a HAP (i.e., qualify as a Section 112 "major source"), but emit less than 100 tons of VOC or PM₁₀, and thus be considered an area source in the national Interim Inventories, and in the CEP inventory.

In order to estimate how much the CEP point/area allocation is likely to differ from the Section 112 definition, the CEP allocations for number of aggregated source categories with a high probability of a discrepancy were examined. These allocations were compared with those in the National Toxics Inventory, discussed above, for which these allocations were estimated on the basis of the Section 112 definition. This cursory comparison suggested that the CEP point/area allocations for chemical manufacturing and refineries may differ significantly from the Section 112 definition, but that the allocations for oil and gas production, electric utilities and industrial boilers probably match the definition reasonably well.

EMISSION PROCESSING OF PRECURSOR SPECIES

Precursors for formaldehyde, acetaldehyde, propionaldehyde, and methyl ethyl ketone (MEK) are modeled in ASPEN as a single precursor species for each secondary species. Differences in secondary product yield and reaction rate were adjusted for in the emission speciation calculation. Product molar yields were assumed to be equal to unity unless specific yield data were available. Reaction rates are from the NIST Chemical Kinetics Database (NIST, 1992).

The prototype precursor for formaldehyde is propene. Reaction rates for each of the other precursors were divided by the rate for propene to obtain the reaction rate ratio. These ratios were multiplied by the formaldehyde yield to obtain the emission scaling factor. Table 3-5 shows the precursors, assumed formaldehyde yields, reaction rate ratios, and emission scaling factors for formaldehyde precursors.

The prototype precursor for acetaldehyde is 2-butene. Reaction rates for each of the other precursors were divided by the rate for 2-butene to obtain the reaction rate ratio. These ratios were multiplied by the assumed acetaldehyde yield to obtain the emission scaling factor. Table 3-6 shows the precursors, assumed acetaldehyde yields, reaction rate ratios, and emission scaling factors for acetaldehyde precursors.

The prototype precursor for propionaldehyde is 2-pentene. Reaction rates for each of the other precursors were divided by the rate for 2-pentene to obtain the reaction rate ratio. These ratios were multiplied by the assumed propionaldehyde yield to obtain the emission scaling factor. Table 3-7 shows the precursors, assumed propionaldehyde yields, reaction rate ratios, and emission scaling factors for propionaldehyde precursors.

The prototype precursor for MEK is 2-methyl-1-butene. Reaction rates for each of the other precursors were divided by the rate for 2-methyl-1-butene to obtain the reaction rate ratio. These ratios were multiplied by the assumed MEK yield to obtain the emission scaling factor. Table 3-8 shows the precursors, assumed MEK yields, reaction rate ratios, and emission scaling factors for MEK precursors.

SPATIAL ALLOCATION OF COUNTY-LEVEL EMISSIONS TO CENSUS TRACTS

The emission processing approach described above produces emissions for area sources and mobile sources at the county level. In order to meet the objectives of this study that relate to determining geographic patterns of exposure, a finer level of resolution is required. A common approach for air quality modeling is to spatially allocate emissions using another geographically distributed variable as a surrogate. For example, each county's emissions from lawn and garden equipment may be allocated to each census tract in proportion to the tract's percentage of residential land area within the county. For many categories of area source emissions, population is the most appropriate surrogate (e.g., residential wood burning, consumer products). For others, land-use categories are more appropriate (e.g., industrial processes, agricultural equipment). Comprehensive land-use data are available from the USGS at 200-meter resolution for 37 categories of land use. An alternative approach, allocation by employment, is hampered by lack of appropriate data at finer than county level.

For this study twenty surrogates, each representing different spatial emissions patterns expected for different emissions source categories, were developed using data on population (Bureau of the Census, 1990a and 1990b), roadway miles and railway miles (Bureau of the Census, 1993), and land use (U.S. Geological Survey) for each census tract.

For the spatial allocation of onroad motor vehicle emissions, we developed a spatial surrogate based upon a composite of roadway miles by roadway type (e.g., freeways, local streets), from the TIGER/Line database, and population. The surrogate gives equal weight to roadway miles and population, under the assumption that the magnitude of vehicle emissions is related to both the availability of roads and the number of people in the area. A further consideration is that onroad vehicle emissions are higher on high-capacity/high-speed roads and on congested/low-speed roads; however, this is accounted for to some degree in the roadway class-specific emission estimates developed by the EPA for the 1990 National Inventory. Similarly, differences between rural and urban counties are already reflected in the 1990 National Inventory.

The spatial distributions of onroad vehicle exhaust and stationary vehicle nonexhaust emissions are different. Exhaust and running loss evaporative emissions occur along vehicle roadways, while hot soak, diurnal, and resting loss evaporative emissions occur where vehicles are parked. The procedure allocates onroad vehicle emissions to a surrogate based on roadways and population. It does not differentiate between exhaust and nonexhaust emissions. This is consistent with current EPA guidance for developing modeling inventories. It is also consistent with the technique used to estimate nonexhaust emissions in the 1990 National Inventory, which is to multiply gram-per-mile evaporative rates by vehicle miles traveled by roadway class.

The spatial surrogates used for allocation of each area and mobile source category are summarized in Table 3-9.

STACK PARAMETERS

Information on stack height, exit temperature and exit velocity for point source emitters are important inputs to the dispersion modeling methodology. Data reported for point sources in the 1990 national VOC and PM₁₀ inventories include stack parameters. However, the TRI database and the TSDf data base do not contain stack parameter information. Values for these facilities were estimated by using the VOC emission-weighted average stack parameters from the 1990 national VOC inventory for facilities with matching SIC codes.

TABLE 3-1. VOC/PM₁₀ emission comparisons between the Int90 and NET90

VOC Emissions					
Source	INT90 (1993 Version)		NET90		Ratio of
	(tons/year)	(% of Total)	(tons/year)	(% of Total)	INT90(93)/NET90
Point	4,326,194	18%	2,574,407	15%	1.68
Area	10,351,323	44%	6,918,407	39%	1.50
Nonroad Mobile	2,117,512	9%	1,957,911	11%	1.08
Onroad Mobile	6,831,412	29%	6,268,323	35%	1.09
Total	23,626,441	100%	17,719,049	100%	1.33
PM ₁₀ Emissions					
Source	INT90 (1995 Version)		NET90		Ratio of
	(tons/year)	(% of Total)	(tons/year)	(% of Total)	INT90(95)/NET90
Point	1,055,933	3%	1,544,685	5%	0.68
Area-Nondust	1,586,487	4%	2,159,085	7%	0.73
Area-Dust	38,032,510	92%	24,789,088	85%	1.53
Nonroad Mobile	336,071	1%	385,822	1%	0.87
Onroad Mobile	354,390	1%	333,190	1%	1.06
Total	41,365,391	100%	29,211,870	100%	1.42

TABLE 3-2. VOC area source emission comparisons between the Int90 and NET90

Source	INT90 (tons/year)	NET90 (tons/year)	Ratio of INT90/NET90	Emission Difference INT90-NET90
Waste Disposal	2,253,578	496,424	4.54	1,757,154
Solvent Utilization	4,858,886	3,510,119	1.38	1,348,768
Industrial Processes	949,313	531,407	1.79	417,906
Storage and Transport	1,267,235	1,031,276	1.23	235,959
Miscellaneous Area Sources	575,239	492,627	1.17	82,612
Natural Sources	0	13,792	0.00	-13,792
Stationary Source Fuel Combustion	447,073	766,712	0.58	-319,638
Total	10,351,323	6,842,355	1.51	3,508,968
Area Source VOC Emissions: Waste Disposal, Treatment and Recovery				
Source	INT90 (tons/year)	NET90 (tons/year)	Ratio of INT90/NET90	Emission Difference INT90-NET90
TSDFs	1,928,828	178,711	10.79	1,750,117
Open Burning	262,655	173,314	1.52	89,341
On-Site Incineration	51,239	35,137	1.46	16,102
Leaking Underground Storage Tanks	0	23,136	0.00	-23,136
Wastewater Treatment	10,855	39,680	0.27	-28,824
Landfills	0	46,446	0.00	-46,446
Total	2,253,578	496,424	4.54	1,757,154
Area Source VOC Emissions: Solvent Utilization				
Source	INT90 (tons/year)	NET90 (tons/year)	Ratio of INT90/NET90	Emission Difference INT90-NET90
Consumer Solvent Utilization	1,442,544	896,511	1.61	546,032
Industrial Adhesives	369,270	98,749	3.74	270,521
Degreasing	683,050	429,108	1.59	253,941
Surface Coating	1,396,386	1,308,157	1.07	88,229
Others	170,197	82,132	2.07	88,065
Dry Cleaning	207,559	127,532	1.63	80,027
Graphic Arts	134,845	100,679	1.34	34,165
Commercial Solvent Utilization	455,037	467,250	0.97	-12,213
Total	4,858,886	3,510,119	1.38	1,348,768

TABLE 3-3. VOC emission comparisons among the Int90 inventory, the NET90 inventory, and the ESD survey.

Source Category	INT90 (tons/year)	NET90 (tons/year)	ESD Survey (tons/year)
General Solvent Utilization	0	198,463	
Personal Care Products	233,903	87,954	290,196
Household Products	183,174	71,398	91,822
Automotive Aftermarket Products	665,065	202,264	177,448
Adhesives and Sealants	360,402	109,299	75,781
Pesticides Application ¹	0	94,965	220,825
Miscellaneous Products	0	132,169	
Total	1,442,544	896,511	856,072

¹ The CEP inventory used the VOC emissions from the ESD survey.

TABLE 3-4. PM₁₀ area dust emission comparisons between Int90 and NET90

Source	INT90	NET90	INT90/ NET90	INT90- NET90
Aircraft Unpaved Airstrips	6,664	6,706	1.0	-42
Paved Roads ¹	5,930,293	2,232,085	2.7	3,698,209
Unpaved Roads ¹	12,206,794	11,120,973	1.1	1,085,821
Wind Erosion Construction ¹	8,245,980	4,192,559	2.0	4,053,421
General Building Construction	129,774	0		129,774
Heavy Construction	21,546	0		21,546
Road Construction	88,273	0		88,273
Geogenic Wind Erosion ¹	4,156,452	2,092,060	2.0	2,064,392
Agriculture Production, Crops Tilling ¹	6,852,135	4,742,995	1.4	2,109,140
Agriculture Production: Livestock	21,756	28,254	0.8	-6498
Agriculture Production: Beef Cattle Feedlot	372,844	373,456	1.0	-613
Total	38,032,510	24,789,088	1.5	13,243,422

¹ PM₁₀ emissions for this category were not used in the CEP inventory.

TABLE 3-5. Emission scaling factors for formaldehyde precursors.

Species	Molar Yield	Reaction Rate Ratio to Propene	Emission Scaling Factor
Ethene	1.6	0.3	0.48
Propene	1	1	1
1-butene	1	1	1
1-pentene	1	1	1
1-hexene	1	1	1
1-heptene	1	1	1
1-octene	1	1	1
1-nonene	1	1	1
1-decene	1	1	1
Isobutene	1	1.6	1.6
(2-methylpropene)			
2-methyl-1-butene	1	1.6	1.6
1,3-butadiene	1	2	2
3-methyl-1-butene	1	1	1
3-methyl-1-pentene	1	1	1
2,3-dimethyl-1-butene	1	1.6	1.6
Isoprene	0.67	3	2
2-ethyl-1-butene	1	1.6	1.6
2-methyl-1-pentene	1	1.6	1.6
4-methyl-1-pentene	1	1	1
2,4,4-trimethyl-1-pentene	1	1.6	1.6
Acetaldehyde	1	0.5	0.5
MTBE	0.42	0.1	0.04
Methanol	1	0.03	0.03

TABLE 3-6. Emission scaling factors for acetaldehyde precursors.

Species	Molar Yield	Reaction Rate Ratio to 2-Butene	Emission Scaling Factor
Propene	1	0.5	0.5
2-butene	2	1	2
2-pentene	1	1	1
2-hexene	1	1	1
2-heptene	1	1	1
2-octene	1	1	1
2-nonene	1	1	1
2-methyl-2-butene	1	1.5	1.5
3-methyl-2-pentene	1	1.5	1.5
4-methyl-2-pentene	1	1	1
Ethanol	1	0.05	0.05

TABLE 3-7. Emission scaling factors for propionaldehyde precursors.

Species	Yield	Reaction Rate Ratio to 2-Pentene	Emission Scaling Factor
1-butene	1	0.5	0.5
2-pentene	1	1	1
3-hexene	2	1	2

TABLE 3-8. Emission scaling factors for MEK precursors.

Species	Molar Yield	Reaction Rate Ratio to 2-Methyl-1-butene	Emission Scaling Factor
2-methyl-1-butene	1	1	1
Butane	1	0.03	0.03
Isopentane	1	0.03	0.03
3-methylpentane	1	0.03	0.03

TABLE 3-9. Surrogates used for proportional allocation of area and mobile source emissions from county level to census tract level.

Surrogate for emissions at census tract level	Definition	Emissions source categories
Population	U.S. Census category: 1990 residential population	Residential heating; architectural coatings; consumer products; non-industrial pesticide application; gasoline service stations; structure fires
1/Population density	Inverse of: census tract population (as defined above) divided by census tract land area as reported by U.S. Census	Recreational vehicles; construction and construction equipment; aircraft; landfills; wastewater treatment
Roadway miles	Total miles of all roadway types in each census tract, as reported in TIGER/Line	Asphalt application
Population/2 + Roadway miles/2	Surrogate based equally on population fraction and on roadway mile fractions for each of four roadway types	On-road mobile source emissions
Railway miles	Total railway miles, as reported in TIGER/Line	Railroads
Residential land	USGS land use categories: "Residential," plus one-third of "mixed urban and built-up land" plus one-third of "other urban and built-up land"	Lawn and garden equipment
Commercial land	USGS land use categories: "Commercial and services," plus one-half of "industrial and commercial complexes," plus one-third of "mixed urban and built-up land" plus one-third of "other urban and built-up land"	Commercial and institutional fuel combustion; commercial equipment; dry cleaners; commercial and institutional incinerators and landfills
Industrial land	USGS land use categories: "industrial," plus one-half of "industrial and commercial complexes," plus one-third of "mixed urban and built-up land," plus one-third of "other urban and built-up land"	Industrial fuel combustion; industrial equipment; chemical manufacturing; metal production and products; wood, rubber and plastics products; industrial coatings; degreasing and solvent utilization; chemical and fuel bulk stations/terminals and pipelines; incineration
Residential and commercial land	Sum of residential land and commercial land, as defined above	Non-industrial asphalt roofing
Commercial and industrial land	Sum of commercial land and industrial land, as defined above	Petroleum and petroleum products storage and transport

(continued)

TABLE 3-9. (concluded) Surrogates used for proportional allocation of area and mobile source emissions from county level to census tract level.

Surrogate for emissions at census tract level	Definition	Emissions source categories
Population/2 + Commercial land/2	Surrogate based equally on fractions of residential population and commercial land use	Non-industrial solvent uses
Utility land	USGS land use category: "transportation, communications, and utilities"	Electric utility fuel combustion
Farmland	USGS land use category: "cropland and pasture"	Farm equipment; agricultural field burning
Orchard land	USGS land use category: "orchards, groves, vineyards, nurseries, and ornamental horticultural areas"	Orchard heaters
Agricultural land	USGS land use categories: farmland and orchard land, as defined above, plus "confined feeding operations" plus "other agricultural land"	Agriculture production
Rangeland	USGS land use categories: "herbaceous rangeland" plus "scrub and brush" plus "mixed rangeland"	Oil and gas production
Forest land	USGS land use categories: "deciduous forest" plus "evergreen forest" plus "mixed forest land"	Logging equipment; forest wildfires
Rangeland and forest land	Sum of rangeland and forest land, as defined above	Prescribed burning
Mining and quarry land	USGS land use category: "strip mines, quarries, and gravel pits"	Mining and quarrying
Water	US Census category: water area	Marine vessels

4 NATIONAL HAP EMISSION INVENTORY

As described in Chapter 3, HAP emissions were developed for 10 separate source categories including point, area, and mobile sources. The categories are:

Point

- Metal manufacturing (SICs between 33 and 34, excluding combustion sources)
- Non-metal manufacturing (includes SIC between 20 and 39, excluding 33, 34, 2911, and combustion sources)
- Refineries (SIC 2911, excluding combustion sources)
- Municipal waste combustors (MWC)
- Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDFs)
- Other (including utility and industrial boilers, coke ovens, and all combustion sources)

Area

- Manufacturing (including chemical manufacturing, food and kindred products, secondary metal production, petroleum refining, wood products, rubber and plastics, industrial surface coating, degreasing, miscellaneous industrial solvent utilization, and industrial adhesive application)
- Nonmanufacturing (including small stationary combustion sources, oil and gas production, construction, non-industrial surface coating, dry cleaning, commercial and consumer solvent utilization, gasoline service stations, on-site incineration, open burning, and wastewater treatment)

Mobile

- Onroad
- Nonroad

This section presents a summary of the national HAP inventory used for this study.

NATIONAL HAP EMISSION TOTALS

A total of 148 target HAPs had non-zero emissions from at least one source category. Table 4-1 presents the HAP emission totals for point sources by source category for the 48-state region. The manufacturing point source and metal totals in this table are taken from the 1990 Toxic Release Inventory. Formaldehyde and acetaldehyde precursors were calculated from reported emissions of ethene and propene, which are reported in the TRI. Dioxin emissions were estimated as described in Attachment 3. Refinery and other point source emissions were derived from the national 1990 VOC and PM₁₀ inventories as described in Chapter 3 and Attachment 3. TSDF emissions were provided by the EPA (Coburn, 1995). The MWC totals were from a separate analysis.

TABLE 4-1. Estimates of 1990 emission totals (tons/day) for toxics and precursors, by source category, for the 48-state region: point sources.

Species	TRI Nonmetal	Refinery	TRI Metal	MWC	TSDF	Other Point	Total Point
Toxics							
Acetaldehyde	9.84	0.959		0.0371		5.73	16.6
Acetamide	4.79e-5						4.79e-5
Acetonitrile	2.05		3.58e-3		0.0541	6.74e-4	2.11
Acetophenone					2.86e-4		2.86e-4
Acrolein	0.0302	0.852		0.0148	0.0175	1.37	2.28
Acrylamide	0.0669		3.43e-4		7.11e-5		0.0673
Acrylic acid	0.590	0.383				0.0837	1.06
Acrylonitrile	4.31	1.48	3.43e-4		8.41e-3	1.67	7.47
allyl chloride	0.281				5.92e-3		0.287
Aniline	0.657	0.393			0.0187	2.19	3.26
Anisidine	2.52e-3						2.52e-3
Antimony compounds	0.0378	0.0538	0.033	0.0796		0.294	0.498
Arsenic compounds	4.53e-3	0.0243	3.47e-3	0.0100		2.66	2.70
Benzene	9.15	24.5	15.8	0.785	0.12	93.7	144
Benzotrichloride	0.0114				8.57e-6		0.0114
Benzyl chloride	0.0459	0.383			7.00e-4	0.0788	0.508
Beryllium compounds	6.84e-6	1.02e-3	1.88e-3	5.57e-4		0.0821	0.0856
Biphenyl	1.53	7.68e-4	1.46e-3			4.42e-3	1.54
bis(2-ethylhexyl) phthalate	1.71	1.31e-4	0.0811		7.60e-3	0.186	1.98
bis(chloromethyl) ether	4.97e-4				8.19e-8		4.97e-4
Bromoform	0.0659	2.44e-3			3.58e-5	0.018	0.0864
1,3-butadiene	6.58	0.139		0.115		8.35	15.2
Cadmium compounds	1.46e-3	5.94e-3	0.0168	0.0388		0.232	0.295
Calcium cyanamide	0.0173				1.36e-5		0.0173
Captan	0.0264						0.0264
Carbaryl	0.0116						0.0116
Carbon disulfide	134	0.102	2.06e-3		0.101	50.6	185
Carbon tetrachloride	2.31	0.460	1.37e-5	1.29e-3	0.322	1.11	4.20
Carbonyl sulfide	25.2	0.0319	8.08e-4			10.6	35.8
Catechol	0.0384						0.0384
Chloramben	1.37e-5						1.37e-5
Chlordane	6.04e-3				2.27e-4		6.27e-3
Chloroacetic acid	0.0345						0.0345
Chlorobenzene	5.54	0.832	7.75e-3	1.77e-3	0.0674	4.35	10.8
Chloroform	30.8	0.396		0.108	0.317	0.752	32.4
Chloromethyl methyl ether	4.57e-3						4.57e-3
Chloroprene	2.14	0.373				0.289	2.80
Chromium compounds	0.136	0.0360	0.425	0.0832		1.32	2.00
Cobalt compounds	0.0245	9.73e-4	0.0271	0.0515		0.212	0.316
Cresol	0.684	0.433	0.658	0.265	0.0526	5.87	7.96
Cumene	3.89	0.435	0.0598	0.117		2.93	7.43
Cyanide compounds	0.865	0.0290	6.91e-4		4.83e-4	0.116	1.01
2,4-D, salts and esters	0.0109				4.05e-3		0.0150
Dibutylphthalate	0.163	0.0563	6.84e-6		3.24e-4	0.0243	0.244
p-dichlorobenzene	1.12	0.819		0.004	0.0645	0.694	2.70
3,3'-dichlorobenzidine	3.42e-5				1.01e-3		1.04e-3
Dichloroethyl ether	5.17e-3				2.64e-8		5.17e-3
1,3-dichloropropene	0.0814				1.58e-3		0.0830
Dichlorvos	1.11e-3						1.11e-3
Diethanolamine	0.234		0.216				0.450
N,N-diethyl/dimethylaniline	0.0699						0.0699
diethyl sulfate	7.52e-3						7.52e-3
3,3'-dimethoxybenzidine	5.47e-6				5.40e-5		5.95e-5
dimethyl formamide		3.08e-3				0.0607	0.0638
1,1-dimethyl hydrazine	6.34e-4				1.02e-3		1.65e-3

Continued.

TABLE 4-1. Continued.

Species	TRI Nonmetal	Refinery	TRI Metal	MWC	TSDF	Other Point	Total Point
dimethyl phthalate	0.085	1.61e-3	0.365		4.82e-6	0.0146	0.466
dimethyl sulfate	0.0133				6.82e-3		0.0201
4,6-dinitro-o-cresol	6.43e-5				1.08e-3		1.14e-3
2,4-dinitrophenol	6.64e-4		0.0332		3.20e-4		0.0342
2,4-dinitrotoluene	0.0788		1.51e-5		0.0145		0.0933
1,4-dioxane	0.802		0.0901		6.91e-3		0.899
Epichlorohydrin	0.504	0.383	3.43e-4		1.09e-5	0.0788	0.966
1,2-epoxybutane	0.109						0.109
ethyl acrylate	0.275	0.516	1.37e-5			0.175	0.966
Ethylbenzene	9.50	4.69	0.677	0.123	0.299	12.4	27.7
ethyl carbamate	5.23e-3				3.76e-4		5.61e-3
ethyl chloride	5.41	0.314	0.124	0.0237		0.319	6.19
ethylene dibromide	0.0754	0.383			8.61e-5	0.154	0.612
ethylene dichloride	7.55	0.618	0.0822		0.496	0.481	9.23
ethylene glycol	13	0.0493	1.69			2.96	17.7
ethylene oxide	2.79	0.0204			3.14e-6	0.424	3.23
ethylene thiourea	3.90e-4				2.93e-9		3.90e-4
ethylidene dichloride					8.02e-5		8.02e-5
Formaldehyde	16.6	7.71	0.383	0.284	0.633	108	134
glycol ethers	35.2	2.13	32.3			2.58	72.2
Heptachlor	5.20e-3				0.0804		0.0856
Hexachlorobenzene	2.01e-3				0.0253		0.0273
Hexachlorobutadiene	6.71e-3				4.32e-3		0.0110
Hexachlorocyclopentadiene	0.116				0.0134		0.129
Hexachloroethane	2.98e-3		8.02e-3		0.0688		0.0798
Hexane		57.1		0.224		42.7	100
Hydrazine	0.0345		1.37e-3		6.29e-3		0.0422
Hydrochloric acid	91.3	6.99	20.0	163		629	910
Hydrofluoric acid	2.46	0.0590	9.68	274		68.6	81.1
Hydroquinone	0.0161						0.0161
lead compounds	0.213	0.0878	0.973	0.640		4.54	6.45
Lindane	2.12e-3				6.49e-4		2.77e-3
Maleic anhydride	0.676	0.0736			2.65e-3	0.0576	0.810
manganese compounds	0.49	0.0418	1.08	0.326		3.07	5.01
mercury compounds	0.0289	3.22e-3	1.38e-3	0.187		0.231	0.452
Methanol	273	2.17	6.19		7.11	26.0	314
Methoxychlor	2.19e-3				03.85e-6		2.19e-3
methyl bromide	4.07				1.79e-3		4.07
methyl chloride	10.6	3.02e-3	0.0455	0.12	0.035	2.03	12.8
methyl chloroform	165	8.99e-3	60.6	0.0326	3.31	6.00	235
methyl ethyl ketone	145	0.785	23.3	0.148	8.68	8.03	186
Methyl hydrazine	1.37e-6				0.02		0.0200
Methyl iodide	0.0408				3.81e-5		0.0408
Methyl isobutyl ketone	32.3	0.711	5.48		0.762	2.20	41.5
Methyl isocyanate	0.0196		6.84e-5		4.09e-3		0.0238
Methyl methacrylate	3.63	0.155	3.43e-4		0.15	3.05	6.99
Methyl tert-butyl ether	1.51	6.82	1.37e-5			10.3	18.6
4,4'-methylene	1.73e-3				6.44e-6		1.74e-3
bis(2-chloroaniline)							
Methylene chloride	122	0.0460	7.66	0.0564	16.5	5.03	151
Methylene diphenyl diisocyanate	0.583	4.94e-7	0.250			9.03e-4	0.834
4,4'-methylenedianiline	0.0268					2.86e-4	0.0271
Naphthalene	2.66	0.572	1.92	0.0879	1.17	2.50	8.91
Nickel compounds	0.283	0.988	0.320	0.104		5.02	6.71
Nitrobenzene	0.09	0.381	6.91e-4		5.16e-3	0.0638	0.541
4-nitrophenol	0.0105				1.74e-5		0.0105
2-nitropropane	0.115				0.0269		0.142

Continued.

TABLE 4-1. Concluded.

Species	TRI Nonmetal	Refinery	TRI Metal	MWC	TSDf	Other Point	Total Point
Parathion	8.39e-4				1.89e-6		8.41e-4
Pentachloronitrobenzene	3.85e-4						3.85e-4
Pentachlorophenol	0.0318				1.71e-3		0.0335
Phenol	6.53	0.440	3.13	0.498	0.107	14.3	25.0
p-phenylenediamine	1.53e-3				4.75e-4		2.01e-3
Phosgene	6.63e-3						0.0066
Phthalic anhydride	0.944	0.223	3.43e-4		0.0546	0.236	1.46
Polychlorinated biphenyls		1.27e-7	6.84e-6	3.97e-3	0.0759	1.43e-5	0.0799
Polycyclic organic matter		2.13		0.381		21.1	23.6
Propionaldehyde	1.35	0.414		8.17e-3		0.598	2.37
Propoxur	2.74e-5						2.74e-5
Propylene dichloride	1.42	0.0197			1.92e-4	0.0158	1.46
Propylene oxide	1.87	0.388	3.49e-4			0.0949	2.35
1,2-propylenimine	8.36e-4						8.36e-4
Quinoline	0.0129		0.0250				0.0379
Quinone	2.19e-3				7.52e-6		2.20e-3
Selenium compounds	1.10e-3	0.214	1.72e-3	1.98e-3		0.804	1.02
Styrene	42.2	0.975	0.463		0.741	16.9	61.3
Styrene oxide	3.32e-3						3.32e-3
PCDD/PCDFs	2.70e-9	2.98e-8		5.24e-6		2.66e-6	7.93e-6
1,1,2,2-tetrachloroethane	0.0614				0.0347		0.0961
Tetrachloroethylene	21.8	7.28e-3	8.64	0.116	1.35	22.3	54.2
Toluene	290	28.7	22.0	0.557	35.3	81.8	458
2,4-toluene diamine	5.38e-3				8.53e-5		5.47e-3
2,4-toluene diisocyanate	0.0708	0.385	6.65e-3		2.68e-3	0.119	0.584
o-toluidine	0.0102		6.84e-6				0.0102
1,2,4-trichlorobenzene	0.509	3.59e-4	6.19e-3		0.459	2.81e-3	0.977
1,1,2-trichloroethane	0.436	2.99e-3	2.84e-3		0.822	0.25	1.51
Trichloroethylene	33	5.54e-3	20.7	0.0489	2.23	7.58	63.6
2,4,6-trichlorophenol	1.07e-4				1.63e-4		2.70e-4
Trifluralin	0.0214						0.0214
2,2,4-trimethylpentane	0	14.1		0.119		13.2	27.4
Vinyl acetate	7.59	0.604				0.531	8.73
Vinyl bromide	0.0138						0.0138
Vinyl chloride	1.55	0.395	7.12e-4	0.098	0.0265	2.73	4.80
Vinylidene chloride	0.416		3.49e-4	4.69e-3	0.173		0.594
Xylene	156	19.9	31.4	0.315	20.3	42.7	271
Total HAPs	1759	196	277	169	102	1367	3870
Precursors^a							
Acetaldehyde precursor	10.6 ^b	16	0.114 ^b	0.176		69.6	96.5
Formaldehyde precursor	40.4 ^b	17.3	0.894 ^b	1.19		200	260
Methyl ethyl ketone precursor		16.2		0.0110		18.9	35.1
Propionaldehyde precursor		4.65		0.0111		12.0	16.7
Total precursors	51	54.2	1.01	1.39		301	408
Coke oven						79.8	79.8

^a Precursor emission totals represent the mass of secondary product that will ultimately form. The actual yield of secondary product that is estimated to form within 50 km of each emission source (the maximum downwind distance simulated) will depend on atmospheric conditions. ^b Includes ethene and propene only.

Area and mobile source totals are presented in Table 4-2. Onroad mobile sources are the largest category in this table, accounting for 34 percent of total area/mobile emissions and 76 percent of total mobile emissions. Area-nonmanufacturing sources are the second largest category, accounting for 35 percent of total area/mobile emissions and 64 percent of area source emissions. These emissions were all derived from the national 1990 VOC and PM10 inventories. The area-nonmanufacturing category primarily reflects small stationary combustion sources, such as coal, oil and wood burning. This category also includes small commercial, industrial, and residential incinerators as well as miscellaneous combustion sources such as forest, brush, and structure fires and prescribed burning. Other sources in

this category are oil and gas production, construction, non-industrial surface coating, dry cleaning, commercial and consumer solvent utilization, and gasoline service stations.

Estimates of total point, total area, and total mobile emissions are summarized in Table 4-3. Total HAP emissions for the 48-state region are 19,625 tons per day. Of this total, 43 percent is from area sources, 37 percent from mobile sources, and 20 percent from point sources. The greatest number of HAPs are associated with point sources (148), followed by area sources (68) and mobile sources (35). Toluene, formaldehyde precursors, xylene, hydrochloric acid, and benzene have the largest emissions by mass. However, because the toxicity of the target HAPs varies widely, comparisons based on mass emissions do not necessarily reflect the relative severity of the hazards posed by each chemical.

TABLE 4-2. Estimates of 1990 emission totals (tons/day) for toxics and precursors, by source category, for 48-state region: area and mobile sources.

Species	Manuf.	Nonmanuf.	Onroad Mobile	Nonroad Mobile	Total Area/ Mobile
Toxics					
Acetaldehyde	16.1	133	88.8	47.6	286
Acrolein	13.0	136	23.7	22.3	195
Acrylonitrile	6.57				6.57
Antimony compounds	0.0491	0.152	1.96e-2	0.0342	0.257
Arsenic compounds	0.0467	0.0960	6.98e-2	0.0818	0.298
Benzene	95.6	357	746	210	1409
Beryllium compounds	1.06e-3	5.10e-3		8.32e-4	7.00e-3
Biphenyl	5.29e-4	1.70e-4			6.99e-4
Bromoform		0.843			0.843
1,3-butadiene		83.9	90.7	43.2	218
Cadmium compounds	0.0134	0.508		2.46e-3	0.524
Carbon disulfide	2.77				2.77
Carbon tetrachloride	5.96	0.720			6.68
Carbonyl sulfide	0.899	0.0833			0.982
Chlorobenzene	20.9	28.0			48.9
Chloroform	13.4	2.21			15.6
Chloroprene	10.5				10.5
Chromium compounds	0.0469	0.462	0.104	0.110	0.729
Cobalt compounds	7.03e-3	0.138	7.74e-3	6.21e-3	0.159
Cresol		27.2	36.8	9.45	73.5
Cumene		12.8	7.68	6.34	26.8
Cyanide compounds			64.0	11.5	75.5
Dibutylphthalate		0.460			0.460
p-dichlorobenzene	22.9	46.5			69.4
1,3-dichloropropene		56.7			56.7
Dimethyl formamide	8.38				8.38
Ethyl acrylate	3.74				3.74
Ethylbenzene	7.07	27.0	234	103	371
Ethyl chloride	8.87	0.355			9.23
Ethylene dichloride	22.5				22.5
Ethylene glycol	12.7	297			310
Ethylene oxide	0.485	1.31			1.80
Formaldehyde	41.4	441	313	178	973
Glycol ethers	193	192			385
Hexane	65.1	268	172	85.3	590
Hydrochloric acid	131	623		8.11	762
Hydrofluoric acid	0.337	7.80		0.577	8.71
lead compounds	0.576	2.49	1.17	0.849	5.17
Maleic anhydride	2.08				2.08
Manganese compounds	0.0704	4.60	0.859	0.431	6.03
Mercury compounds	2.60e-3	0.239	0.0194	0.0176	0.279

Continued.

TABLE 4-2. Concluded.

Species	Manuf.	Nonmanuf.	Onroad Mobile	Nonroad Mobile	Total Area/ Mobile
Methanol	25.6	549	20.1	19.6	614
Methyl chloride	0.0693	9.75			9.82
Methyl chloroform	542	427			969
Methyl ethyl ketone	274	164	15.4	3.25	457
Methyl isobutyl ketone	112	16.3			128
Methyl methacrylate	2.98				2.98
Methyl tert-butyl ether	33.5	37.0	229	83.0	383
methylene chloride	144	20.9			165
Naphthalene	0.0774	24.8	85.7	22.9	133
nickel compounds	0.103	3.37	0.185	0.707	4.38
Phenol	10.7	49.5	44.5	8.53	113
phthalic anhydride	6.3	0.0987			6.40
polychlorinated biphenyls		2.05e-4			2.05e-4
polycyclic organic matter	0.886	53.1	102	22.4	178
Propionaldehyde	1.38	2.63	16.0	11.0	31.0
Propylene dichloride	0.554				0.554
Propylene oxide	0.138				0.138
Selenium compounds	0.0455	0.274	5.69e-3	7.08e-3	0.333
Styrene	27.1	0.785	38.4	9.26	75.5
PCDD/PCDFs	1.26e-7	1.66e-6	1.46e-7	1.49e-7	2.08e-6
Tetrachloroethylene	45.3	219			264
Toluene	378	719	1580	368	3045
1,1,2-trichloroethane		0.198			0.198
Trichloroethylene	161	1.21			162
2,2,4-trimethylpentane		56.4	595	122	773
Vinyl acetate	17				17.0
Vinyl chloride	11.1	1.47			12.6
Xylene	543	415	929	358	2245
Total HAPs	3043	5522	5434	1756	15755
Precursors^a					
Acetaldehyde precursor	26.2	303	721	204	1254
Formaldehyde precursor	66.4	863	1530	577	3036
Methyl ethyl ketone precursor	6.93	86.6	158	28.6	280
Propionaldehyde precursor	3.29	89.5	186	47.3	326
Total precursors	103	1342	2595	857	4897
Diesel PM ₁₀			681	673	1395
Gasoline PM ₁₀			291	116	431

^a Precursor emission totals represent the mass of secondary product that will ultimately form. The actual yield of secondary product that is estimated to form within 50 km of each emission source (the maximum downwind distance simulated) will depend on atmospheric conditions.

There are 79 HAPs for which the only identified emissions are from point sources. These species are primarily chemical intermediates that have no uses outside the chemical industry. For an additional 26 HAPs, point source emissions exceed area and mobile emissions. Some of these species are also chemical intermediates, as well as metals and dioxin for which the main sources are large stationary combustion sources. For 14 HAPs and all four HAP precursors, mobile sources are the largest contributor to total emissions. Finally, for 29 HAPs, area sources are the largest contributors. These HAPs are primarily solvents, although some combustion products are also included.

TABLE 4-3. Summary estimates of 1990 emission totals (tons/day) for toxics and precursors, by source category, for the 48-state region.

Species	Total Point	Total Area	Total Mobile	Total
Toxics				
Acetaldehyde	16.6	149	136	302
Acetamide	4.79e-5			4.79e-5
Acetonitrile	2.11			2.11
Acetophenone	2.86e-4			2.86e-4
Acrolein	2.28	149	46	197
Acrylamide	0.0673			0.0673
Acrylic acid	1.06			1.06
Acrylonitrile	7.47	6.57		14.0
Allyl chloride	0.287			0.287
Aniline	3.26			3.26
Anisidine	2.52e-3			2.52e-3
Antimony compounds	0.498	0.201	0.0538	0.753
Arsenic compounds	2.70	0.143	0.152	3.00
Benzene	144	453	956	1553
Benzo(1,2,3-cd)pyrene	0.0114			0.0114
Benzyl chloride	0.508			0.508
Beryllium compounds	0.0856	6.16e-3	8.32e-4	0.0926
Biphenyl	1.54	6.99e-4		1.54
Bis(2-ethylhexyl) phthalate	1.98			1.98
Bis(chloromethyl) ether	4.97e-4			4.97e-4
Bromoform	0.0864	0.843		0.929
1,3-butadiene	15.2	83.9	134	233
Cadmium compounds	0.295	0.521	2.46e-3	0.819
Calcium cyanamide	0.0173			0.0173
Captan	0.0264			0.0264
Carbaryl	0.0116			0.0116
Carbon disulfide	185	2.77		188
Carbon tetrachloride	4.20	6.68		10.9
Carbonyl sulfide	35.8	0.982		36.8
Catechol	0.0384			0.0384
Chloramben	1.37e-5			1.37e-5
Chlordane	6.27e-3			6.27e-3
Chloroacetic acid	0.0345			0.0345
Chlorobenzene	10.8	48.9		59.7
Chloroform	32.4	15.6		48.0
Chloromethyl methyl ether	4.57e-3			4.57e-3
Chloroprene	2.80	10.5		13.3
Chromium compounds	2.00	0.509	0.214	2.7
Cobalt compounds	0.316	0.145	0.0139	0.474
Cresol	7.96	27.2	46.3	81.4
Cumene	7.43	12.8	14.0	34.3
Cyanide compounds	1.01		75.5	76.5
2,4-D, salts and esters	0.0150			0.0150
Dibutylphthalate	0.244	0.460		0.704
p-dichlorobenzene	2.70	69.4		72.1
3,3'-dichlorobenzidine	1.04e-3			1.04e-3
Dichloroethyl ether	5.17e-3			5.17e-3
1,3-dichloropropene	0.0830	56.7		56.8
Dichlorvos	1.11e-3			1.11e-3
Diethanolamine	0.450			0.450
N,N-diethyl/dimethylaniline	0.0699			0.0699
Diethyl sulfate	7.52e-3			7.52e-3
3,3'-dimethoxybenzidine	5.95e-5			5.95e-5
Dimethyl formamide	0.0638	8.38		8.44
1,1-dimethyl hydrazine	1.65e-3			1.65e-3

Continued

TABLE 4-3. Continued.

Species	Total Point	Total Area	Total Mobile	Total
dimethyl phthalate	0.466			0.466
dimethyl sulfate	0.0201			0.0201
4,6-dinitro-o-cresol	1.14e-3			1.14e-3
2,4-dinitrophenol	0.0342			0.0342
2,4-dinitrotoluene	0.0933			0.0933
1,4-dioxane	0.899			0.899
epichlorohydrin	0.966			0.966
1,2-epoxybutane	0.109			0.109
ethyl acrylate	0.966	3.74		4.71
ethylbenzene	27.7	34.1	337	399
ethyl carbamate	5.61e-3			5.61e-3
ethyl chloride	6.19	9.23		15.4
ethylene dibromide	0.612			0.612
ethylene dichloride	9.23	22.5		31.7
ethylene glycol	17.7	310		327
ethylene oxide	3.23	1.80		5.03
ethylene thiourea	3.90e-4			3.90e-4
ethylidene dichloride	8.02e-5			8.02e-5
formaldehyde	134	482	491	1107
glycol ethers	72.2	385		457
Heptachlor	0.0856			0.0856
hexachlorobenzene	0.0273			0.0273
hexachlorobutadiene	0.0110			0.0110
hexachlorocyclopentadiene	0.129			0.129
hexachloroethane	0.0798			0.0798
hexane	100	333	257	690
hydrazine	0.0422			0.0422
hydrochloric acid	910	754	8.11	1672
hydrofluoric acid	81.1	8.14	0.577	90
hydroquinone	0.0161			0.0161
lead compounds	6.45	3.07	2.02	11.5
Lindane	2.77e-3			2.77e-3
maleic anhydride	0.810	2.08		2.89
manganese compounds	5.01	4.67	1.29	10.97
mercury compounds	0.452	0.242	0.0370	0.730
Methanol	314	575	39.7	929
Methoxychlor	2.19e-3			2.19e-3
methyl bromide	4.07			4.07
methyl chloride	12.8	9.82		22.7
methyl chloroform	235	969		1204
methyl ethyl ketone	186	438	18.7	643
methyl hydrazine	0.0200			0.0200
methyl iodide	0.0408			0.0408
methyl isobutyl ketone	41.5	128		170
methyl isocyanate	0.0238			0.0238
methyl methacrylate	6.99	2.98		9.97
methyl tert-butyl ether	18.6	70.5	312	401
4,4'-methylene bis(2-chloroaniline)	1.74e-3			1.74e-3
methylene chloride	151	165		316
methylene diphenyl diisocyanate	0.834			0.834
4,4'-methylenedianiline	0.0271			0.0271
naphthalene	8.91	24.9	109	142
nickel compounds	6.71	3.47	0.892	11
nitrobenzene	0.541			0.541
4-nitrophenol	0.0105			0.0105
2-nitropropane	0.142			0.142
Parathion	8.41e-4			8.41e-4

Continued

TABLE 4-3. Concluded.

Species	Total Point	Total Area	Total Mobile	Total
Pentachloronitrobenzene	3.85e-4			3.85e-4
Pentachlorophenol	0.0335			0.0335
Phenol	25.0	60.2	53.0	138
p-phenylenediamine	2.01e-3			2.01e-3
Phosgene	6.63e-3			6.63e-3
phthalic anhydride	1.46	6.40		7.86
polychlorinated biphenyls	0.0799	2.05e-4		0.0801
polycyclic organic matter	23.6	54.0	124	202
Propionaldehyde	2.37	4.01	27.0	33.4
Propoxur	2.74e-5			2.74e-5
propylene dichloride	1.46	0.554		2.01
propylene oxide	2.35	0.138		2.49
1,2-propylenimine	8.36e-4			8.36e-4
Quinoline	0.0379			0.0379
Quinone	2.20e-3			2.20e-3
selenium compounds	1.02	0.320	0.0128	1.36
Styrene	61.3	27.9	47.7	137
styrene oxide	3.32e-3			3.32e-3
PCDD/PCDFs	7.93e-6	1.79e-6	2.95e-7	1.00e-5
1,1,2,2-tetrachloroethane	0.0961			0.0961
Tetrachloroethylene	54.2	264		319
Toluene	458	1097	1950	3505
2,4-toluene diamine	5.47e-3			5.47e-3
2,4-toluene diisocyanate	0.584			0.584
o-toluidine	0.0102			0.0102
1,2,4-trichlorobenzene	0.977			0.977
1,1,2-trichloroethane	1.51	0.198		1.71
Trichloroethylene	63.6	162		226
2,4,6-trichlorophenol	2.70e-4			2.70e-4
Trifluralin	0.0214			0.0214
2,2,4-trimethylpentane	27.4	56.4	717	801
vinyl acetate	8.73	17.0		25.7
vinyl bromide	0.0138			0.0138
vinyl chloride	4.80	12.6		17.4
vinylidene chloride	0.594			0.594
Xylene	271	958	1287	2516
Total HAPs	3870	8565	7190	19625
Precursors^a				
acetaldehyde precursor	96.5	329	925	1351
formaldehyde precursor	260	929	2107	3296
methyl ethyl ketone precursor	35.1	94	187	315
Propionaldehyde precursor	16.7	93	233	343
Total precursors	408	1445	3452	5305
Diesel PM ₁₀			1354	1354
Gasoline PM ₁₀			407	407
coke oven	79.8			79.8

^a Precursor emission totals represent the mass of secondary product that will ultimately form. The actual yield of secondary product that is estimated to form within 50 km of each emission source (the maximum downwind distance simulated) will depend on atmospheric conditions.

An important difference between the area/mobile sources and the point sources is that area/mobile sources tend to be distributed relatively evenly throughout urban areas. Thus, despite large emission totals, concentrations may be relatively low and have limited variability from one location to the next. Point source emissions, by contrast, are more concentrated. The national totals in some cases may represent emissions from only a handful of locations. In these cases, high concentrations can occur in near-source locations even if the national emission totals seem relatively small.

Another important difference is that point sources are often elevated, so that emissions are subject to dispersion before reaching ground level. Because area and mobile source emissions are more typically released at ground level, emissions from these source types at a given location will often result in higher ground level concentrations than an equal magnitude of emissions from point sources.

It is important to view these totals in context with their uncertainties. The level of uncertainty varies by source category, and was estimated to be the lowest for onroad mobile sources and the highest for manufacturing point sources. Uncertainties are also different for individual HAPs within a source category.

Table 4-4 presents estimates of PM₁₀-derived HAP emission totals for the 48-state region, showing the contributions of fine and coarse PM₁₀ to the totals in Tables 4-1 to 4-3. Table 4-4 also lists totals for dust-related sources, which are not included in Tables 4-2 and 4-3. Dust is by far the largest source category for most PM₁₀-derived HAPs. Because of our concerns regarding the accuracy of the dust estimates, the great majority of these emissions were not modeled. Non-dust emissions for all HAPs are primarily in the fine fraction, with the percent fine ranging from 55 percent for antimony to 91 percent for diesel PM₁₀. For a few source categories, size-specific speciation profiles were available. However, for most source categories, the fine and coarse speciation profiles were the same, and the percent fine was determined by the relative emissions of PM_{2.5} and PM₁₀ in the inventory.

HAP GROUPS

Toxic metal measurements of emissions from anthropogenic sources are generally characterized as totals of all metal compounds. Because of availability of data in this form, emission estimates for this study have been similarly characterized. However, because the toxicology of various compounds containing a given metal atom may differ significantly, analysis of environmental health implications of emissions would be improved by distinguishing the various compounds with speciation analysis. Attachment 6 summarizes information about the speciation of several toxic metal compounds:

- Beryllium compounds,
- Chromium compounds,
- Manganese compounds,
- Mercury compounds, and
- Nickel compounds.

Polycyclic organic matter (POM), defined as all organic compounds containing 2 or more fused benzene rings, is also discussed in Attachment 6. Families of homologous organic chemicals, such as POM, are collections of distinct organic chemical species that are grouped in emission inventories because they share certain structural features that causes them to exhibit similar chemical behavior so that such chemicals are almost always observed as complex mixtures. The precise composition of the mixture in which such compounds are emitted is determined by a combination of the conditions under which they originally formed and the conditions to which they are subjected prior to emission.

TABLE 4-4. Estimates of 1990 PM₁₀-derived HAP emission totals (tpd) by source category, for the 48-state region.

Species	Size	Onroad			Nonroad			Area, Non-manuf.			Area, Dust			TRI			TRI			Total PM ₁₀ and pct Fine (w/o dust)		
		Mobile	Mobile	Mobile	Mobile	Mobile	Mobile	Manufac.	Non-manuf.	Non-manuf.	Area, Dust	Area, Dust	Area, Dust	Refinery	Metal ^a	Metal ^a	MWC	Other Point	Other Point			
Arsenic	fine	0.0629	0.0681	0.0335	0.0335	0.0335	0.0335	0.0335	0.0335	0.0335	0.0335	0.0335	0.0335	0.0179	0.0035	0.0009	0.0009	1.55	3.00			
	coarse	0.0069	0.0137	0.0132	0.0132	0.0132	0.0132	0.0132	0.0132	0.0132	0.0132	0.0132	0.0132	0.0064	0.0001	0.0001	0.0001	1.11	(60% fine)			
Beryllium	fine		3.21e-4	7.27e-4	7.27e-4	7.27e-4	7.27e-4	7.27e-4	7.27e-4	7.27e-4	7.27e-4	7.27e-4	7.27e-4	5.81e-4	0.0019	5.01e-4	5.01e-4	0.0568	0.0926			
	coarse		5.11e-4	3.37e-4	3.37e-4	3.37e-4	3.37e-4	3.37e-4	3.37e-4	3.37e-4	3.37e-4	3.37e-4	3.37e-4	4.41e-4		5.7e-5	5.7e-5	0.0253	(68% fine)			
Cadmium	fine		9.15e-4	0.0092	0.0092	0.0092	0.0092	0.0092	0.0092	0.0092	0.0092	0.0092	0.0092	0.0038	0.0168	0.0349	0.0349	0.150	0.819			
	coarse		0.0015	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042	0.0021		0.0039	0.0039	0.0823	(76% fine)			
Chromium	fine	0.0894	0.088	0.0327	0.0327	0.0327	0.0327	0.0327	0.0327	0.0327	0.0327	0.0327	0.0327	0.0163	0.425	0.0749	0.0749	0.949	2.72			
	coarse	0.0144	0.022	0.0142	0.0142	0.0142	0.0142	0.0142	0.0142	0.0142	0.0142	0.0142	0.0142	0.0197		0.0083	0.0083	0.370	(72% fine)			
Cobalt	fine	0.0063	0.0056	0.0046	0.0046	0.0046	0.0046	0.0046	0.0046	0.0046	0.0046	0.0046	0.0046	3.69e-4	0.0271	0.0464	0.0464	0.170	0.474			
	coarse	0.0014	0.0006	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	6.04e-4		0.0051	0.0051	0.0415	(80% fine)			
Lead	fine	0.8964	0.743	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.0560	0.973	0.576	0.576	3.00	11.5			
	coarse	0.2748	0.106	0.156	0.156	0.156	0.156	0.156	0.156	0.156	0.156	0.156	0.156	0.0318		0.064	0.064	1.54	(75% fine)			
Manganese	fine	0.5542	0.341	0.0537	0.0537	0.0537	0.0537	0.0537	0.0537	0.0537	0.0537	0.0537	0.0537	0.0254	1.08	0.293	0.293	2.07	10.97			
	coarse	0.3048	0.090	0.0167	0.0167	0.0167	0.0167	0.0167	0.0167	0.0167	0.0167	0.0167	0.0167	0.0164		0.033	0.033	1.00	(67% fine)			
Nickel	fine	0.1527	0.345	0.0637	0.0637	0.0637	0.0637	0.0637	0.0637	0.0637	0.0637	0.0637	0.0637	0.594	0.32	0.0934	0.0934	3.20	11.08			
	coarse	0.0318	0.362	0.039	0.039	0.039	0.039	0.039	0.039	0.039	0.039	0.039	0.039	0.394		0.0104	0.0104	1.82	(59% fine)			
Selenium	fine	0.0057	0.0063	0.0419	0.0419	0.0419	0.0419	0.0419	0.0419	0.0419	0.0419	0.0419	0.0419	0.211	0.0017	1.78e-3	1.78e-3	0.691	1.35			
	coarse		7.65e-4	0.0036	0.0036	0.0036	0.0036	0.0036	0.0036	0.0036	0.0036	0.0036	0.0036	0.0029		1.98e-4	1.98e-4	0.113	(90% fine)			
Antimony	fine	0.0134	0.0128	0.0366	0.0366	0.0366	0.0366	0.0366	0.0366	0.0366	0.0366	0.0366	0.0366	0.0314	0.033	0.0716	0.0716	0.142	0.753			
	coarse	0.0061	0.0214	0.0125	0.0125	0.0125	0.0125	0.0125	0.0125	0.0125	0.0125	0.0125	0.0125	0.0224		0.0080	0.0080	0.152	(55% fine)			
Gasoline	fine	181	95																407			
PM ₁₀	coarse	110	21																(68% fine)			
Diesel PM ₁₀	fine	616	620																1354			
	coarse	65	53																(91% fine)			

^a TRI emissions are not identified as fine and coarse fractions and were modeled as 100% fine.

EMISSION TOTAL COMPARISONS

The estimates of emission totals provided in Tables 4-1 through 4-4 were compared to other available national emission estimates. These include estimates for motor vehicle-related HAPs (benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and diesel particulate matter) (EPA, 1993c), mercury (EPA, 1995a), dioxin (EPA, 1994b), and cadmium (Jones et al., 1993a). In addition, total emissions of several solvents were compared to total 1990 sales, under the assumption that the ultimate fate of these compounds is predominantly release to the atmosphere.

Solvents

Table 4-5 compares the 48-state preliminary estimates of 1990 emissions of five solvents with total U.S. sales information (USITC, 1991). These are species that are highly volatile, such that their ultimate fate is likely to be release to the atmosphere. In addition, they are not generally produced in combustion. Therefore, it is reasonable to expect that total emissions will be similar to total sales. Exceptions to this could occur if significant fractions of the amount sold in a given year was stockpiled rather than used immediately, or if large amounts were recycled, burned, or released to the groundwater. The agreement between total emissions and total sales is very good for three of the five solvents.

TABLE 4-5. Comparison of estimates of total emissions (tpd) of five solvents with total 1990 sales.

Species	Total 1990 U.S. Emissions	Total 1990 U.S. Sales	Emissions as a Percent of Sales
methylene chloride	316	389	81
methyl chloroform	1204	931	129
methyl ethyl ketone	643	637	101
methyl isobutyl ketone	170	147	116
Tetrachloroethylene	319	510	63

Motor Vehicle-Related HAPs

Table 4-6 compares estimates of 48-state onroad mobile source emission totals with values presented in the EPA *Motor Vehicle-Related Air Toxics* report to Congress (EPA, 1993c). That study used mobile emission factors for VOC HAPs obtained from a model (MOBTOX) that was based on MOBILE4.1, whereas the present study used an inventory based on the newer version, MOBILE5. For diesel PM₁₀, the present study used emission factors derived from the PART5 model; the earlier study had used a different approach since PART5 had not been released at that time. Emission totals for VOC HAPs in the present study would be expected to be approximately 30 percent higher than those in the EPA study due to the higher emission factor predictions in MOBILE5. Table 4-6 shows that the totals for the present study are 7 to 56 percent higher.

The values obtained in the present study are expected to be more accurate since they are based on actual average speeds by roadway type and seasonal average temperatures and VMT from counties throughout the nation, rather than on a single set of conditions. In

addition, the present study included regional variation in gasoline composition, which should lead to more accurate emission estimates for benzene and the aldehydes.

TABLE 4-6. Comparison of estimates of 1990 48-state and EPA (1993c) emission totals (Mg/yr) for motor vehicle-related HAPs.

Species	48-State Total	EPA (1993c)
Benzene	247,000	158,000
1,3-butadiene	30,000	28,000
Formaldehyde	104,000	74,000
Acetaldehyde	29,000	21,000
diesel particulate matter	226,000	163,000

Mercury

A comparison of mercury emissions for the national HAP inventory to a national mercury inventory reported by EPA (1995a) is presented in Table 4-7. There is a good agreement between the inventories in overall estimates: 0.73 tons/day in the CEP inventory and 0.68 tons/day in the EPA's Draft Mercury Report to Congress (RTC) inventory. As shown in Table 4-7, the estimated emissions from point sources are lower in the CEP inventory than the EPA inventory, and emissions from area sources are higher. The differences may be due, at least in part, to different source allocations in the inventories.

As shown in Table 4-7, the estimated mercury emissions are dominated by the point sources in both inventories. There is a good agreement between the inventories for two major point source categories: municipal waste incineration (0.19 tons/day in the CEP inventory vs. 0.15 tons/day in the EPA inventory), and coal combustion (0.18 tons/day in the CEP inventory vs. 0.20 tons/day in the EPA's Draft Mercury RTC inventory). However, there is a poor agreement between the estimates for metal production (0.0028 tons/day in the CEP inventory vs. 0.045 tons/day in EPA inventory). The poor agreement for medical waste incinerators is likely explained by the inclusion of the bulk of these emissions in the area source incineration category in the CEP inventory. The small contribution from medical waste incinerator point sources in the CEP inventory is derived from estimates of 0.027 tons/day PM₁₀ emissions for this category in the national PM₁₀ inventory. (Note that this estimate was revised to 0.20 tons/day in the National Emissions Trends inventory, discussed in Chapter 3.)

A summary of the estimated emissions comparisons disaggregated to states is presented in Table 4-8. The state level comparison shows that the inventory estimates are within a factor of 2 for 92 percent of the states (45 states), and within a factor of 1.3 for 47 percent of the states (23 states). There are seven states among the those with the highest emissions in both inventories: New York, Texas, Ohio, Pennsylvania, Illinois, Michigan, and Florida. In the CEP inventory Tennessee, Massachusetts, and Maryland complete the list; the corresponding states in the EPA inventory are Missouri, California, and New Jersey.

A summary of the estimated mercury emissions disaggregated among 3,113 counties is presented in Table 4-9. The results show that the inventories are within a factor of 2 for more than half the counties (1,582), and within a factor of 5 for 84 percent of the counties (2,618).

TABLE 4-7. Comparison of estimates of mercury emission totals (tons/day) in the current study to those from the draft 1995 EPA Mercury Report to Congress.

Source Category	48-State Total (1990)	EPA (1995) ^a
Manufacturing sources	0.052	0.089
Refineries	0.0030	NE ^b
Metal production	0.0028	0.045
Lead	0.00090	0.024
Other	0.046	0.044
Combustion point sources	0.40	0.57
Coal	0.18	0.20
Oil	0.0030	0.028 ^c
MWC	0.19	0.15
MedWI	0.0016 ^d	0.18
Other	0.023	0.010
Mobile sources	0.037	NE
Area sources	0.24	0.021
Incinerators	0.21	NE
Residential wood combustion	0.015	NE
Other	0.018	0.021
TOTAL	0.73	0.68

^a No year given; however, it is post-1991. ^b Not estimated; data considered insufficient. ^c The more recent utility study (EPA, 1995b) gives a much lower value (0.00069 tons/day) for utility oil boilers; the inventory in this study was scaled to match this value. ^d The majority of the emissions from medical waste incineration are included in the area source incineration category.

TABLE 4-8. State level comparisons of mercury emission estimates (emissions in tons/day)

State	CEP Inventory	EPA Inventory	CEP-to-EPA Ratio
ratios > 2 (3 states and DC)			
DC	0.009	0.001	9.00
NV	0.004	0.001	4.00
ID	0.003	0.001	3.00
TN	0.032	0.015	2.13
2 ≥ ratios > 1.5 (8 states)			
SD	0.002	0.001	2.00
MD	0.028	0.015	1.87
KS	0.009	0.005	1.80
OR	0.007	0.004	1.75
WA	0.014	0.008	1.75
AZ	0.010	0.006	1.67
NM	0.005	0.003	1.67
WI	0.016	0.010	1.60
1.5 ≥ ratio > 1.3 (6 states)			
DE	0.003	0.002	1.50
MS	0.006	0.004	1.50
UT	0.006	0.004	1.50
OH	0.044	0.030	1.47
NE	0.004	0.003	1.33
TX	0.050	0.038	1.32

Continued

TABLE 4-8. Concluded.

1.3 \geq ratio $>$ 1 (12 states)			
IA	0.010	0.008	1.25
SC	0.010	0.008	1.25
WY	0.005	0.004	1.25
NY	0.057	0.047	1.21
AR	0.006	0.005	1.20
AL	0.020	0.017	1.18
MA	0.028	0.024	1.17
IL	0.031	0.028	1.11
KY	0.014	0.013	1.08
NC	0.014	0.013	1.08
MI	0.029	0.027	1.07
IN	0.025	0.024	1.04
ratio = 1 (6 states)			
CO	0.006	0.006	1.00
CT	0.013	0.013	1.00
MN	0.016	0.016	1.00
OK	0.007	0.007	1.00
RI	0.001	0.001	1.00
VT	0.001	0.001	1.00
1 $>$ ratio $>$ 0.75 (5 states)			
GA	0.016	0.017	0.94
LA	0.009	0.010	0.90
NJ	0.023	0.027	0.85
ME	0.005	0.006	0.83
MT	0.005	0.006	0.83
0.75 \geq ratio $>$ 0.5 (8 states)			
WV	0.009	0.012	0.75
CA	0.021	0.030	0.70
VA	0.014	0.020	0.70
PA	0.037	0.053	0.70
ND	0.004	0.006	0.67
NH	0.002	0.003	0.67
FL	0.027	0.043	0.63
MO	0.017	0.031	0.55

TABLE 4-9. County level comparisons of mercury emission estimations

Range of CEP-to-EPA Ratios	Number of Counties	Percent of Counties
$>$ 100	11	0.35
$100 \geq$ Ratios $>$ 50	7	0.22
$50 \geq$ Ratios $>$ 10	92	2.96
$10 \geq$ Ratios $>$ 5	194	6.23
$5 \geq$ Ratios $>$ 2	667	21.43
$2 \geq$ Ratios $>$ 1	961	30.87
Ratios = 1	18	0.58
$0.5 \leq$ Ratios $<$ 1	603	19.37
$0.2 \leq$ Ratios $<$ 0.5	369	11.85
$0.1 \leq$ Ratios $<$ 0.2	86	2.76
$0.01 \leq$ Ratios $<$ 0.1	68	2.18
Ratios $<$ 0.01	30	0.96
Estimated emissions = 0	7	0.22

Table 4-10 lists the 10 counties in each inventory with the greatest emissions, and the largest source category contributor for each. There are three counties listed for both inventories: Cook, IL, Baltimore City, MD and Essex, MA. Municipal waste combustors are the largest contributors to most of the listed counties in both inventories, although the emissions are greater in the CEP inventory than the EPA inventory.

TABLE 4-10. Top 10 county level mercury emissions in the CEP and EPA inventories

County	Emission (tons/day)	Largest Source Contributor
EPA Inventory		
Jefferson, MO	0.014	primary lead smelters: 0.0139 tons/day
Cook, IL	0.014	Sec mercury prod: 0.004 tons/day; MWC: 0.0024 tons/day
Los Angeles, CA	0.010	MWC: 0.0026 tons/day
Wayne, MI	0.009	MWC: 0.005 tons/day
Essex, NJ	0.009	MWC: 0.003 tons/day; sec mercury prod.: 0.004 tons/day
Alachua, FL	0.008	MWC: 0.0067 tons/day
Iron, MO	0.007	primary lead smelters: 0.0068 tons/day
Dade, FL	0.007	MWC: 0.0045 tons/day
Baltimore City, MD	0.007	MWC: 0.005 tons/day
Essex, MA	0.007	MWC: 0.0058 tons/day
CEP Inventory		
Baltimore City, MD	0.020	MWC: 0.019 tons/day
New York, NY	0.020	MWC: 0.019 tons/day
Essex, MA	0.015	MWC: 0.013 tons/day
Philadelphia, PA	0.012	MWC: 0.011 tons/day
Westchester, NY	0.011	MWC: 0.010 tons/day
Grimes, TX	0.011	Other Point: 0.011 tons/day
Hillsborough, FL	0.010	MWC: 0.009 tons/day
Cook, IL	0.010	MWC: 0.007 tons/day
Washington, DC	0.009	MWC: 0.007 tons/day
Fairfield, CT	0.009	MWC: 0.008 tons/day

Cadmium

The EPA "Locating and Estimating Air Emissions" document (L&E) for cadmium contains a national cadmium inventory (Jones et al., 1993a). Table 4-9 presents a comparison of the 48-state emission totals from the present study to the totals in the L&E report for cadmium. The L&E report concluded that coal-fired power plants were responsible for the majority of cadmium emissions nationwide. These estimates were based primarily on mass-balance considerations and the cadmium content of coal. However, the more recent Utility study (EPA, 1995b) reported direct measurements of cadmium emissions from coal- and oil-fired utility boilers and found them to be much smaller than the earlier estimates. The values used in the present study were scaled to match the Utility study totals for utility boilers; the national totals are higher because they include industrial boilers. Despite the much lower totals for utility boilers, the overall emission total for the present study are similar to the Jones study, because of the much greater emission estimates for area sources, especially prescribed burning.

TABLE 4-11. Comparison of estimates of cadmium emission totals (Mg/yr) in the current study to those from the 1993 EPA L&E Report.

Source Category	48-State Total, 1990	Jones et al. (1993) ^a
Manufacturing sources	60	48.4
Refineries	2.0	NE ^b
Metal production	56	32.9
Lead	11.3	14.3
Zinc	7.4	7.2
Cement	2.9	3.0
Other	0.5	12.5
Combustion point sources	36	259
Coal	2.2	218 ^c
Oil	6.0	28.6 ^c
MWC	12.9	7.0
Other	15.2	5.4
Mobile sources	0.8	NE
Area sources	173	NE
Incinerators	35	NE
Prescribed burning	126	NE
Other	12	NE
TOTAL	270	307

^a Emissions for 1990. ^b Not estimated; data considered insufficient. ^c The more recent Utility study gives a much lower value (1.9 Mg/yr for utility coal boilers; the inventory in the present study was scaled to match this value).

Dioxin

Two recent studies have provided estimates of national dioxin emissions: the EPA draft dioxin study (EPA, 1994b) and a study conducted by the Center for the Biology of Natural Systems (CBNS) at Queens College (Cohen et al., 1995). In Table 4-10 the estimates of total dioxin emissions for the present study are compared with those from the other inventories. The methodology used in the present study did not capture the emissions from medical waste incinerators (MeWI) well because these emissions are generally not included in the point source portion of the national PM₁₀ inventory. MeWI are one of the largest source categories for dioxin in both of the other inventories. The differences between the inventory totals in the present study and those in the other inventories are largely due to the MeWI category. However, the current EPA estimate of dioxin emissions from MeWI has been reduced from the value in the draft report.

TABLE 4-12. Comparison of estimates of dioxin emission totals (g/yr as TEQ) in the current study to those from the 1994 EPA report and the 1995 CBNS study.

Source Category	48-State Total (1990)	EPA (1994)	Cohen (1995) ^a
Manufacturing sources, total	576	580	1,000
Refineries	10	NE ^b	NE
Metal production, total	215	232	490
Lead	1.6 ^c	1.6	NE
Copper	213 ^c	230	280
Iron/Steel	NE	NE	210
Cement	351	350	510
Other	0	NE	NE
Combustion point sources, total	2,052	8,500	6,600
Coal	175	NE ^d	200
Wood	49 ^c	320	230 ^e
MWC	1,737	3,000	1,900
MeWI	7.1 ^f	5,100	4,200
Other	84	63	96
Mobile sources, total	98	88	123
Area sources, total	592	126	NE
Incinerators	481	NE	NE
Residential wood combustion	40 ^c	40	NE
Forest fires	29	86	NE
Other	42	NE	NE
TOTAL	3,318	9,300	7,800

^a Emissions for 1993. ^b Not estimated. ^c Scaled to match EPA inventory. ^d The more recent utility study (EPA, 1995b) gives a value of 140 g/yr for utility coal boilers; inventory in present study was scaled to match this value). ^e Includes residential wood combustion. ^f The majority of the emissions from medical waste incineration are included in the area source incineration category.

5 ASPEN MODEL FORMULATION, SPECIFICATIONS, AND UNCERTAINTIES

This chapter describes the general structure and formulation of the ASPEN model and its predecessors, and presents the model specifications of the ASPEN model along with a discussion of the associated uncertainties.

MODEL STRUCTURE AND FORMULATION

The Assessment System for Population Exposure Nationwide (ASPEN) consists of three separate modules:

1. A dispersion module estimates ambient concentration increments at a set of fixed receptor locations in the vicinity of an emission source (i.e., the receptor grid).
2. A mapping module interpolates ambient concentration increment estimates from the grid receptors to census tract centroids, and sums contributions from all modeled sources.
3. An exposure module estimates the average concentration increment to which the population of a census tract is exposed, accounting for time spent in indoor and outdoor microenvironments and time spent in other census tracts.

The dispersion and mapping module are used to estimate air toxics concentrations in this study and are described in this chapter; the exposure module is under development and is discussed in a separate document (Rosenbaum, 1996).

The ASPEN dispersion module, like its predecessors the Human Exposure Model (HEM) and the South Coast Risk and Exposure Assessment Model - Version 2 (SCREAM2), uses a Gaussian model formulation and climatological data to estimate long-term average concentrations. For each source, the model calculates ground-level concentrations as a function of radial distance and direction from the source for a set of receptors laid out in a radial grid pattern. These concentrations represent the steady-state concentrations that would occur with constant emissions and meteorological parameters. This calculation uses vertical dispersion coefficients (σ_z) that are functions of the atmospheric stability. Stability categories range from A (very unstable) to F (very stable). In an unstable atmosphere, vertical mixing is rapid. Unstable conditions occur at midday, when air near the ground is warmer than air above. In a stable atmosphere, vertical mixing is suppressed. Stable conditions occur at night, when ground-level air is cooler than air above.

For each grid receptor, concentrations are calculated for each combination of stability class, wind speed, and wind direction. These concentrations are averaged together using the annual frequency of occurrence of each stability/wind speed/wind direction combination for that receptor as weightings. The resulting output of ASPEN's dispersion module is a grid of annual average outdoor concentration estimates for each source/pollutant combination.

As explained below, the meteorological frequency distributions are normally prepared for the entire simulation period, usually one or more years. For ASPEN, however,

meteorological data are stratified by time of day. This is done to preserve any characteristic diurnal patterns that might be important in the subsequent estimation of population exposure, since population activity patterns may also display characteristic diurnal patterns. Thus, there is a frequency distribution for each daily time block, which represents the annual distribution of meteorological conditions during that time of day, and a corresponding diurnal set of annual average concentration estimates for each source/pollutant combination.

These diurnally stratified annual average concentration estimates from ASPEN's dispersion module are then interpolated from the grid receptors to census tract centroids with ASPEN's mapping module, and contributions from all modeled sources are summed to give estimates of cumulative ambient concentration increments in each census tract. By accounting for all identified source categories (including background concentrations) in this project, the sum of the concentration increments should yield an estimate of the overall concentration of each HAP within each census tract. These estimates are designed to represent population-weighted concentration averages for each census tract, as explained below.

MODEL SPECIFICATIONS AND UNCERTAINTIES

Gaussian Dispersion Formulation

Plume rise and dispersion parameters and formulations from the HEM model were modified to assure consistency with those in the ISCLT2 model (EPA, 1992b), which was recommended by the EPA for estimating long-term average concentrations resulting from both urban and rural emission sources in simple terrain at the time this study began (EPA, 1987a). Parallel simulations were made with the ASPEN dispersion module and ISCLT2 under a variety of conditions to confirm consistency.

Uncertainties

The use of Gaussian models with climatological data is the standard regulatory approach for characterizing long-term exposures. However, this approach is recognized as having several major uncertainties. In short-term applications, Gaussian modeling tends to produce conservative (i.e., high) concentration estimates because small-scale fluctuations in wind direction, that tend to reduce peak concentrations, are not accounted for. On the other hand during unstable conditions plumes from tall stacks may descend to ground level more quickly than estimated by the model due to large-scale convective eddies, resulting in underestimates of peak ground level concentrations. Short-term model predictions are generally considered to be no more accurate than a factor of two (e.g., Grisinger and Marlia, 1994), although EPA modeling guidelines (EPA, 1987a) state that the uncertainties in the highest estimated concentrations are 10 to 40 percent. However, the guidelines further note that "estimates of concentrations that occur at a specific time and *place* are poorly correlated with observed concentrations and are much less reliable [*italics added*]," in part due to uncertainties in knowledge of wind parameters affecting plume locations as noted above. The guidelines also state that Gaussian models are more reliable for estimating longer time-averaged concentrations than for estimating short-term concentrations at specific locations. One study found long-term averages to be generally accurate to within 6 percent (Gratt and Levin, 1995).

Like all Gaussian dispersion models, for each scenario ASPEN assumes a steady wind speed and wind direction over the entire modeled fetch of the plume, which is 50 km for this study, the maximum distance recommended by the EPA for application of a Gaussian model. This assumption may be unrealistic in many areas, especially where complex terrain is present, where land use changes abruptly, or near water bodies, even at downwind distances of 50 km or less. ASPEN, like ISCLT, uses a sector averaging approach for lateral dispersion, ameliorating some of the uncertainty in spatial distribution introduced by using a discrete set of wind directions. Also, because ambient concentrations tend to be highest near the source, the uncertainty in spatial distribution of concentrations that is due to the assumption of steady wind speed and direction over an entire 50-km fetch tends to be lowest where concentrations are highest.

Another limitation of the steady-state assumption is that it does not allow for situations where the plume may turn back on itself, as during light and variable winds. This restriction may lead to underestimates of peak concentrations. However, this meteorological condition generally occurs infrequently, so that annual average concentrations would not be significantly affected.

Urban/Rural Dispersion Parameters

Urban environments generally have rougher surfaces that lead to increased wind turbulence, steeper vertical gradients in wind speed, and greater instability than rural environments. For elevated sources, the result is that for identical meteorological variables, urban conditions result in a lower plume rise and greater vertical and horizontal plume dispersion. Because of the lower plume rise, the urban plume may impact ground level concentrations closer to the source than a rural plume with correspondingly less time for dispersion, but with an offsetting increased dispersion rate. The peak ground level concentration may, therefore, be higher or lower in an urban environment, depending on the particular meteorological conditions. However, because of the higher dispersion rate, the spatial average concentration over the plume is generally lower for an urban plume. For ground-level sources, the greater vertical mixing in urban areas leads to lower ground-level concentrations than for a comparable source in a rural area. The exception to this general rule is the case of "A" stability, for which rural dispersion is more rapid than urban. However, "A" stability occurs infrequently.

Thus, the selection of the appropriate dispersion parameters requires characterization of each census tract as urban or rural. EPA modeling guidelines suggest two methods for making this determination: one based on land use and one based on residential population density (urban if greater than 750 people/km²). Although the first is considered more definitive, the latter was implemented because of its lower resource requirements. In cases where census tracts were very small (less than 0.03 km²), so that population density estimates might be misleading, the predominant U.S. Census designation for the block groups contained within the tract was used.¹ There are only 316 such tracts nationwide. Out of the 60,803 census tracts in the modeling domain, our approach resulted in 28,314 urban tracts and 32,489 rural tracts. Of these, the census designation for the majority of block groups within the tract was "urban" for approximately 10,000 tracts which the population density approach designated

¹ The U.S. Census designations are based on different criteria so that urban fringe areas are included in the urban definition, although the surface roughness may be more like rural areas. Therefore, the census designations were only used when the primary approach failed.

as rural. The census designation was rural for approximately 100 tracts that the population density approach designated as urban (excluding the very small tracts for which the population density approach was not used).

Table 5-1 shows the characteristics of the census tracts categorized as urban and rural for this study. As the table shows, the distribution of population size is similar for urban and rural tracts, with rural tracts somewhat smaller, except at the lower end of the distribution. The distribution of area is quite different, however between urban and rural tracts. Ninety percent of urban tracts are 5 km² or smaller, while only about 10 percent of rural tracts are that small. Approximately 75 percent of rural tracts are larger than virtually any urban tract.

TABLE 5-1. Distribution of population size and area among urban and rural census tracts. (Excludes 135 tracts with no population or area.)

%TILE	Population			Total Area (km ²)		
	All Tracts	Urban	Rural	All Tracts	Urban	Rural
1	0	526	0	0.012	0.099	0.003
5	739	1354	143	0.2	0.2	1.3
10	1492	1849	1073	0.6	0.3	4.6
25	2560	2747	2381	1.7	0.9	11.5
50	3762	3897	3637	5.6	1.8	48.9
75	5230	5378	5090	60.1	3.1	211.6
90	6931	7105	6763	294.5	5	512.7
95	8143	8338	7979	542.9	6.3	942.1
99	11523	11653	11407	2155	9.7	3084.1
mean	4072.2	4282.5	3888.1	130.5	2.3	242.6
number	60,668	28,314	32,354	60,668	28,314	32,354
sum	247,051,600	121,255,048	125,796,544	7,916,647	66,126	7,850,521

Uncertainties

Uncertainty in the urban/rural designation is likely to result in some significant uncertainty in ground level ambient concentration estimates, especially for census tracts where population density is not a good indicator of surface roughness (e.g., highly industrial with little residential), or where surface roughness is intermediate (e.g., some suburban residential). The fact that our approach tended to characterize more tracts as rural means that average modeled concentrations for those tracts are likely to be higher than they would be had the census designation been used.

Spatial Resolution and Treatment of Major Point Sources

HEM and SCREAM2 allow a choice as to the spatial resolution of population for exposure assessment: block groups or census tracts for HEM and blocks, block groups, or census tracts for SCREAM2. Due to computational considerations for the nationwide scope of this study, a census-tract resolution was selected for ASPEN. Thus, ambient concentration increments estimated by ASPEN's dispersion module for grid receptors are interpolated to census-tract (population) centroids with log-log interpolation in the radial direction and linear interpolation in the azimuthal direction. As noted above, the estimates are designed to represent population-weighted average concentration for the tract. The implication of this procedure and resolution for exposure assessment is the assumption that either (a) all

population activity in a census tract occurs at the tract centroid, or (b) the concentration does not vary much throughout the tract.

The exception to this procedure is the "resident" census tract, i.e., the tract in which the source is located). Near sources, where ambient concentration gradients are likely to be steep, the position of a tract centroid relative to the source may result in a significant over- or underestimate of the population-weighted average exposure concentration in the tract. The coarser the spatial resolution of the population, the more significant the uncertainty in the average exposure concentration is likely to be. Therefore, for tracts with centroids close to a major point source, the ambient concentration is estimated in ASPEN by spatial averaging of the ambient concentrations of receptors estimated to fall within the bounds of the tracts, instead of by interpolation to the centroid. That is, instead of estimating the ambient concentration increment at a single point in the tract (i.e., at the centroid), the average concentration increment over the entire area of the tract is estimated for the resident tract. Since inclusion of detailed information on the boundaries of the census tracts was judged to be excessively resource-intensive, a circle of equal area to the census tract, centered at the centroid, was used as an estimate of the tract boundary in the spatial averaging procedure. That procedure is implemented as follows.

- For each point source, the tract with the closest centroid is determined, i.e., the resident tract is defined.
- An effective or pseudo-radius is calculated for the resident tract based on the known tract area and the assumption that the shape of the tract is circular.
- Each modeling receptor for the source is evaluated to determine if it falls within the pseudo-radius of the tract.
- Based on the configuration and spacing of the modeling receptors, an area of representation is assigned to each receptor.
- The resident tract's average outdoor concentration is calculated as the area-weighted average of the modeling receptors that fall within its pseudo-radius.

The implication of this treatment is the assumption that population activity within the resident tract is uniformly distributed over the tract.

Uncertainties

Dispersion modeling studies of more limited scope than this study frequently use a greater degree of spatial resolution, e.g., blocks or block groups. The spatial resolution of census tracts in this study raises two types of concerns:

1. Are the population-weighted average tract concentrations accurately estimated by the procedures described?
2. Do population-weighted average tract concentrations constitute valuable information without a corresponding estimate of the distribution of concentrations throughout the tract? That is, should more attention be paid to the potentially high concentrations near point sources, rather than the more aggregate population-weighted tract averages, in order to contribute to our understanding of population exposure to air toxics?

The first concern was addressed as part of the sensitivity analysis in the 54-tract area of Greenpoint/Williamsburg in New York City, described in Attachment 4. For area, onroad

mobile, and nonroad mobile emission sources, spatial resolution at finer than tract level is unwarranted, since the emissions from these source categories tend to be relatively widely dispersed and/or their actual locations are not known. However, for point sources, whose locations may be specified more exactly, it may be possible to estimate ambient concentrations at the resolution of census blocks or block groups. Such an estimate can serve as an alternative means of estimating the population-weighted average exposure concentration for the tract, to which tract level concentration estimates may be compared. The findings of the sensitivity analysis, for which concentration estimates were made at the census block level of resolution, suggested that:

- The spatial averaging procedure for census tract resolution should be limited to resident tracts (i.e., the tract with the closest centroid to each source), because for nearby tracts concentration estimation by interpolation to centroids provided a closer match to the population-weighted average of constituent blocks;
- With spatial averaging limited to resident tracts, for resident and nearby tracts the ASPEN concentration estimate is about 27 percent higher on average than the population-weighted average concentration of the constituent blocks (mean ratio of tract/block—average of 1.27; stdev 0.38; range 0.56 to 1.63), and
- The remaining tract-level estimates are in good agreement with those built up by averaging concentration estimates of constituent blocks (mean ratio of tract/block—average of 0.99; stdev 0.6; range 0.86 to 1.28).

The discrepancy between the tract concentration estimate and the one built up from the constituent block estimates for resident and nearby tracts may be the result of either inaccurate block concentration estimates (due to uncertainties in dispersion parameters near sources or inaccuracies in the interpolation procedure near sources) or inaccurate tract concentration estimates (due to invalidity of the uniform population distribution assumption underlying the spatial averaging procedure) or both. Alternatives to address this discrepancy include (1) retaining the original approach, (2) conducting the analysis of point sources at a finer (i.e., block) level of resolution and estimating tract concentrations with the population-weighted average of constituent blocks, and (3) scaling the ASPEN concentration estimates to try to approximate the value that would have been obtained with modeling at block level resolution. Alternative 1 was selected because it seems more consistent with EPA modeling guidance cautions against use of Gaussian estimates very near sources, and requires significantly lower computer resource costs (there are about 60,000 census tracts and about 7,000,000 blocks).

The long-term population-weighted average concentration is an indicator of the relative risk among census tracts and source types for a given HAP and can highlight those geographic areas and sources warranting further attention. However, to gain a better understanding of the variation of exposure concentrations within tracts, we investigated ways of characterizing intra-tract variability in outdoor concentrations with an estimate of the standard deviation among the blocks within a tract. One approach is based on modeling, as described in Attachment 4. To evaluate the intra-tract variation in outdoor concentrations at the location of populations, the population-weighted means and standard deviations were estimated for census blocks contained within each of the 53 populated tracts in the sensitivity study area. The results suggest that the standard deviation is related to the mean concentration, and that for typical resident and nearby tracts the standard deviation was approximately 35 percent of the mean concentration, while for other tracts the standard

deviation was approximately

5 percent of the mean concentration. Another approach to making this estimate is based on evaluation of observed data, as described in Attachment 5. Observed annual average concentration data for six HAPs from six closely spaced monitors were evaluated for mean concentration and standard deviation. The monitors were sited around a major refinery in Minnesota, so that they could be considered in close proximity to a point source of three of the HAPs and out of close proximity for the remaining three. The standard deviations for the three near-source HAPs agreed well with those predicted by the block level modeling analysis described in Attachment 4, but were considerably higher than those predicted for one of the other HAPs. This finding supports the use of the modeling approach for estimating spatial variability in outdoor concentrations in census tracts near a major point source.

Treatment of Motor Vehicle and Area Sources

We initially identified three options for simulating air quality impacts of area sources (including motor vehicles). The first is the modified "box" model option in SCREAM2. For widely distributed community sources, emission density gradients are assumed to be small; thus, dispersion is assumed to be dominated by vertical processes and by the mean transport wind past the ground level source areas. Concentrations at any point are thus proportional to the local grid emission density ($\text{g}/\text{m}^2/\text{s}$) and inversely proportional to the subregional wind speed and mixing depth. This treatment is, effectively, "box model" dispersion adjusted for the local emission density. The vertical dispersion constant used is based on that in the Gifford and Hanna (1973) urban regional box model. The authors estimated dispersion constants for particles for 44 U.S. urban areas. SCREAM2 uses the average of these values. The primary advantage of this approach is the minimal computational requirements. The primary disadvantage is that horizontal transport between tracts is not treated, which may yield overestimates of ambient concentration gradients where emission gradients are large.

A second option is to represent the motor vehicle and area sources as a single pseudo-point source located at the centroid of each census tract. Outside of the resident census tract of the pseudo-point source, resulting ambient concentration estimates would be interpolated to tract centroids, as is done for major point sources. However, the default interpolation approach could not be implemented within the resident census tract, since the concentration cannot be estimated at the emission point (the tract centroid) with the Gaussian formulation. That is, the population would be assumed to reside precisely at the emission source. Therefore, the model algorithms would be modified so that an estimate of the spatial average ambient concentration within the tract resulting from the pseudo-point source is assigned to the tract population, as is done in the case of the resident tracts for major point sources, discussed above. As in that case, the implication of this treatment would be that the population of the resident census tract is uniformly distributed over the tract, rather than all residing at the centroid. The primary advantage of this approach is that inter-tract transport is addressed, which may be important when emission gradients are large. The primary disadvantage is significantly increased computational requirements.

A third option is to represent motor vehicle and area sources as multiple pseudo-point sources geographically dispersed throughout the census tract, rather than a single source as described in option two, with population exposure to the resulting ambient concentrations estimated as in option two. The primary advantages of this approach are that (1) inter-tract

transport is addressed, in contrast to approach one, and (2) population exposure may be better represented than with approach two, especially in the resident census tract, because emissions are expected to be widely dispersed with small gradients. The primary disadvantage is increased computational requirements.

Uncertainties

The accuracy of the pseudo-point source approach (option 2) for the treatment of area sources (including nonroad and onroad mobile sources) was investigated by comparing ASPEN model predictions using one pseudo-point source with predictions obtained using many, smaller pseudo-point sources, for both urban and rural tracts. The results suggested that nonresident tracts that are moderately removed from the resident centroid are little affected by the number of pseudo-point sources used to represent an area source. Similarly, the results suggest that large resident tracts are not significantly affected. However, for the smaller resident tract, typical for an urban area, the estimated ambient concentration appears to be significantly reduced by increasing the number of pseudo-point sources used to represent the area source. Therefore, for census tracts with areas larger than approximately 0.03 square kilometers (the area encompassed by the innermost receptor ring, as explained below), ambient concentrations in the resident census tract are estimated on the basis of five dispersed pseudo-point sources in ASPEN, with spatial averaging of the ambient concentrations of receptors estimated to fall within the bounds of the tract. This number was selected as the minimum for which concentration estimates converged (i.e., the estimate did not change significantly with additional pseudo-point sources). For tracts smaller than the second innermost modeling receptor ring, spatial averaging with a single pseudo-point source is used. Interpolation of ambient concentrations to the centroids of tracts other than the resident tract is based on a single pseudo-point source in both cases, because there is little difference in the results and computing time is reduced. However, tracts whose centroids are very close to the resident centroid (distance less than the pseudo-radius of the resident tract), and are therefore likely to be influenced by the area source in a similar manner, are also assigned the ambient concentration of the resident tract, instead of estimating the ambient concentration from interpolation.

Temporal Resolution

As explained above, ASPEN estimates annual average outdoor concentrations, stratified by time of day. Modeling inputs, such as frequencies of meteorological conditions, mixing heights, emissions, and reactive decay correspondingly represent annual averages stratified by time of day. Although ASPEN's predecessor, SCREAM2, is designed to make separate ambient and exposure concentrations for each hour of the day, for ASPEN we reduced the number of time blocks from 24 to 8, decreasing computing requirements while still retaining important diurnal variations in emissions, meteorology, and reactive decay. We divided the day into eight 3-hour time blocks. Emissions, meteorological inputs, reactive decay coefficients, and population activity data (used in the exposure module) are all expressed as 3-hour averages. Modeled ambient concentrations for each time block will be used in the exposure phase of this project.

Uncertainties

Because meteorological mixing heights vary seasonally, and the relationship between ambient concentrations and mixing heights in Gaussian modeling is not linear, it is possible for the use of annual average mixing height values to introduce bias into annual average concentration estimates, particularly if emissions also vary significantly by season. The results of the sensitivity analysis described in Attachment 4 found no evidence of any significant bias, even when emissions varied seasonally.

Seasonal stratification of ambient concentrations may be required in order to make unbiased estimates of annual exposure concentrations, since there are also seasonal differences in activity patterns. This issue is addressed in the draft exposure assessment methodology (Rosenbaum, 1996).

Radial Grid Receptor Network

ASPEN uses a polar receptor grid of 12 concentric rings, each with 16 equally spaced receptors (192 receptors total). The ring radii are 0.1, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 40.0, and 50.0 km. As noted above, 50 km is the maximum distance recommended by the EPA for application of a Gaussian model (EPA, 1992b).

Reactive Decay

ASPEN models atmospheric transformation processes as first-order reactive decay. Secondary formation is obtained as the difference between secondary precursor concentrations with and without reactive decay. Two reactive decay pathways are considered: reaction with OH radical, and reaction with NO₃ radical. Reaction with OH is included because it is the major pathway for atmospheric transformation for most HAPs; reaction with NO₃ is included because it can be an extremely rapid pathway at nighttime, when reaction with OH is slow.

Because Gaussian models assume that ambient concentrations at each receptor are proportional to the emission rate for a given set of meteorological conditions, the ASPEN model is designed to simulate the impacts of each point source for a standard emission rate (i.e., 1 g/s). If more than one pollutant is emitted by the same source, the receptor concentrations of each pollutant can then be estimated on the basis of a single dispersion simulation by simple scaling of concentrations with respect to emission rates, assuming that both pollutants have the same deposition and/or reactivity characteristics.

To simulate air quality impacts of the many species addressed in this study, HAPs were classified according to their chemical properties (see Table 2-1). Particulate matter, which is subject to deposition, is treated separately from gaseous pollutants (discussed below). Similarly, pollutants formed in the atmosphere (secondary pollutants) are treated separately (discussed below). The remaining gaseous pollutants are classified into six groups according to their rates of reactive decay. Those classified as "very low" reactivity are modeled as inert, and all others are modeled with reactive decay. Each pollutant within a group is assumed to decay at the same rate. The reactivity categories, typical species included, and their associated OH and NO₃ rate constants are given in Table 5-2. Rate constants for the NO₃ reaction are only provided for the "very high" reactivity category. Although nearly all HAPs in this category react rapidly with NO₃, the same is not true for the other reactivity categories.

For ASPEN, separate decay factors were developed for each time block and stability class, since stability class is largely a function of solar radiation intensity and would be expected to correlate well with atmospheric reactivity. Concentrations of OH and NO₃ were obtained from the OZIPM-4 photochemical box model with the CBM4 chemical mechanism (Hogo and Gery, 1988). In order to develop nationally applicable values, a VOC concentration of 50 ppbC with VOC composition described by EPA default values for transported (regional) air quality was used with a NO_x concentration of 2 ppb. Modeled nighttime OH concentrations of 0.005 ppt were assumed to apply to all stability categories. Summer photolysis conditions were used to derive all OH concentrations for "A" stability, as well as concentrations for all daytime stability categories for the 0600–0900 and 1800–2100 time blocks. Conditions representative of the vernal equinox were used for the other daytime stability categories. The results are presented in Tables 5-3 and 5-4.

Two other major pathways for reactive decay are reaction with ozone and photolysis. These pathways were not explicitly considered because their inclusion would have necessitated breaking the reactivity classes into more subgroups. However, in some cases species that react with ozone rapidly or photolyze rapidly were assigned to a higher reactivity category. For example, formaldehyde has an OH rate constant of 2.6E-4. It would normally be classified in the "low-medium" reactivity category (Table 5-2); however, formaldehyde also photolyzes, and inclusion of photolysis essentially doubles its rate of decay. Therefore, formaldehyde is included in the "medium" reactivity category.

TABLE 5-2. Reactivity categories and associated rate constants.

Category	Typical HAPs	k_{OH} (ppt ⁻¹ s ⁻¹)	k_{NO_3} (ppt ⁻¹ s ⁻¹)
Very high	acetaldehyde precursor, 1,3-butadiene, cresol, MEK precursor, propionaldehyde precursor	1.4 E-3	2.4 E-6
High	aniline	2.4 E-3	0
Medium	chloroprene, formaldehyde precursor, maleic anhydride	9.6 E-4	0
Medium high	acetaldehyde, acrolein, formaldehyde, MIBK, naphthalene, phenol, propionaldehyde, xylene	4.8 E-4	0
Medium low	ethylbenzene, glycol ethers, toluene, vinylidene chloride	1.9 E-4	0
Low	cumene, ethylene glycol, hexane, biphenyl, methyl ethyl ketone, tetrachloroethylene, 1,1,2-trichloroethane, trichloroethylene, vinyl bromide	9.5 E-5	0

TABLE 5-3. Estimated OH concentrations (ppt) as a function of stability category and time block.

Time Block	A	B	C	D	E	F
0000–0300	NA*	NA	NA	0.005	0.005	0.005
0300–0600	NA	NA	0.005	0.005	0.005	0.005
0600–0900	0.06	0.04	0.02	0.01	0.005	0.005
0900–1200	0.4	0.3	0.2	0.1	0.005	0.005
1200–1500	0.34	0.26	0.18	0.1	NA	NA
1500–1800	0.12	0.09	0.06	0.04	0.005	0.005
1800–2100	NA	0.01	0.01	0.005	0.005	0.005
2100–2400	NA	NA	NA	0.005	0.005	0.005

* Not applicable; these combinations of stability and time block do not occur.

TABLE 5-4. Estimated NO₃ concentrations (ppt) as a function of stability category and time block.

Time Block	A	B	C	D	E	F
0000-0300	NA	NA	NA	200	200	200
0300-0600	NA	NA	10	100	200	200
0600-0900	0.5	0.5	0.5	16.7	200	200
0900-1200	0.3	0.3	0.3	0.3	0.3	0.3
1200-1500	0.3	0.3	0.3	0.3	NA	NA
1500-1800	0.5	0.5	0.5	16.7	0.3	0.3
1800-2100	NA	10	10	100	200	200
2100-2400	NA	NA	NA	200	200	200

Uncertainties

Because of the approximate nature of the reactivity classifications, an analysis of the sensitivity of modeling results to reactivity classification is included in Attachment 4. The analysis suggests that for most cases, changing the reactivity classification of a HAP by one category changes the resulting ambient concentration estimates at the census tract centroids by only 0 to 8 percent, about 3 percent on average. The exception to this finding is the addition of an NO₃ decay pathway to the OH pathway for the "very high" classification, which results in concentration estimates lower by 34 percent on average than those estimated on the basis of the next lower reactivity classification.

An additional uncertainty pertains to the estimate of OH concentrations. Although the values presented in Table 5-3 should be applicable over a fairly broad range of conditions, the two variables considered, stability category and time block, are obviously not adequate to fully characterize the range of atmospheric conditions. Actual OH concentrations also vary according to atmospheric levels of NO_x, VOC, ozone, and water vapor, and may be higher or lower than the estimated values for any given situation. However, on an average basis the uncertainty in these values is believed to be low.

Secondary Formation

Chapter 2 identified several toxics that are formed in atmospheric reactions. A subset of these were selected for modeling. Four species were added to the list of compounds to be modeled that represent nontoxic precursors for the toxic species formaldehyde, acetaldehyde, propionaldehyde, and methyl ethyl ketone. Other listed HAPs are also precursor species (butadiene, toluene, and vinylidene chloride). Each precursor-product pair was modeled using the appropriate precursor reactive decay rate. ASPEN calculates the secondary product concentration as the difference between the precursor concentration in an inert model run and its concentration in the presence of reactive decay. The resulting concentration differences are adjusted for molar yield and molecular weight to estimate the concentration of the secondary HAP.

Deposition

Deposition of pollutants onto surfaces reduces average ambient concentrations. This effect may be significant for particles. Dry deposition for most gas-phase HAPs is slow, however, so that for most of these species deposition is less important than chemical reaction as a

removal mechanism (e.g., Ligocki et al., 1991), and neglecting deposition has little effect on modeled concentrations. Exceptions are highly acidic species such as hydrochloric acid (HCl) and polar compounds such as formaldehyde and cresol. Therefore, deposition is accounted for in ASPEN for particulate-phase HAPs but neglected for gas-phase HAPs.

Dry deposition rates for particles are primarily a function of particle size, and are much larger for coarse particles (those with diameters between 2.5 and 10 μm) than for fine particles (those smaller than 2.5 μm). Deposition of coarse particles is primarily a result of gravitational settling. However, for fine particles, deposition is a more complex phenomenon that depends upon the amount of turbulence in the atmospheric layers near the surface. We modeled fine and coarse PM as separate species to capture the large difference in deposition characteristics. Dry deposition rates are also a function of land-use type, and are different for urban and rural environments, and over water. Deposition velocities for the fine and coarse particle modes for urban, rural, and water were obtained from the deposition algorithm used in the UAM-V photochemical model (SAI, 1993), parameterized as a function of stability class and wind speed. In comparison, to estimate deposition with ISCLT2, the user is required to supply a reflection coefficient as a function of settling velocity and ground surface type for each particle size.

A final issue relates to those species that can partition between the gas and particulate phases in the atmosphere. These include POM, PCBs, many pesticides, and dioxin (see Table 2-1). These species were modeled as an inert gas (nondepositing species) for this study, which may result in some overestimation of concentrations.

The wet deposition algorithm from the revised version of the CAP88-PC model was incorporated into ASPEN to address wet deposition of particles. It is based on an approximate method described by Rohde (1980) that uses the fraction of time during which precipitation is occurring in conjunction with the total annual precipitation to calculate both the decay rate for the modeled ambient concentration and deposition flux. (EPA's new short-term model, ISCST3, includes a wet deposition algorithm, but neither ISCLT2 nor ISCLT3 has this feature.)

Mixing Heights

As in ISCLT2, mixing heights are used by the ASPEN model to limit the vertical dispersion of pollutants. Near sources and under very stable (nighttime) conditions, the mixing height has little effect on modeled concentrations because the vertical extent of the plume is determined by the Gaussian plume dispersion algorithms. Further from the source and under unstable (afternoon) conditions, the mixing height has a more significant effect on modeled concentrations. For example, under A stability (characteristic of summer afternoons), modeled plumes expand to a depth of 3000 m within 1–2 km of the source, whereas under F stability plumes do not reach a mixing height of 500 m within 50 km of the source. During D stability, which is generally the most prevalent condition for both day and night, modeled plumes expand to a depth of 1000 m within 20 km of the source. Once a modeled plume has expanded sufficiently to become well-mixed, modeled pollutant concentrations are inversely proportional to the mixing height.

Twice-daily mixing height estimates for 1990 and 1991 for 63 upper-air monitoring sites located throughout the United States are available from the EPA's Support Center for Regulatory Air Models Bulletin Board Service (SCRAM BBS). These data are made

available by the EPA for use with regulatory models such as ISC. We obtained the data and processed them to estimate annual average mixing heights stratified by time of day into 3-hour time blocks.

Uncertainties

Because of the large amount of data required for this national study, the processing procedure was greatly simplified compared to that prescribed by the EPA for regulatory applications (RAMMET data processing software), with corresponding differences in the resulting estimates. The effect of these differences on the resulting model predictions of outdoor concentrations was investigated with parallel simulations for a set of point sources in EPA Region II, as described in Attachment 4. The results suggest that differences in mixing height estimation methodologies make virtually no difference in predicted long-term average outdoor concentrations.

Wind/Stability (STAR) Data

To reduce computing requirements, ASPEN utilizes a climatological modeling approach. As with other climatological models (e.g., the EPA's CDM and ISCLT), the dispersion module is supplied with a **ST**ability **AR**ray (STAR) joint probability matrix. A STAR matrix describes the joint frequency distribution of hourly meteorological measurements sorted into classes, or bins, by wind speed, wind direction, and atmospheric stability. The long-term concentration is calculated by simulating the average concentration for each meteorological bin and summing the averages across bins, weighting each by its frequency of occurrence.

By normal convention, a single STAR matrix is prepared for the entire simulation period, usually one or more years. For ASPEN, meteorological data were prepared in 3-hour time blocks. For example, there is a STAR matrix for the time period from 3 a.m. to 6 a.m., reflecting the relative long-term frequency of each meteorological condition for that time of day. Data were processed for each of the 214 surface meteorological stations in the nationwide WBAN database within the 48-state region that had complete data available for 1990, with the same EPA processor used to create STAR matrices for ISCLT and other climatological dispersion models.

Uncertainties

Due to limitations in available meteorological data (214 stations to represent conditions for the conterminous U.S. provided by the EPA), for many emission sources plume dispersion is estimated on the basis of data from a somewhat distant location that may not accurately represent local conditions. An estimate of this uncertainty is presented in Attachment 4, which describes a set of modeling sensitivity analyses carried out for the Greenpoint/Williamsburg area of New York City. The results suggest that for a typical tract, if all other uncertainties in the estimated concentrations were eliminated, the predicted concentration would be within about 30 percent of the true concentration with 95 percent confidence.

Distance Limitations

As the use of ISCLT or any Gaussian model is not recommended by the EPA at downwind distances beyond 50 km, this limitation was observed in this project. For concentration estimates at long-range transport distances, an approach should be followed that addresses issues that are important at such distances. These issues include:

- Wet and dry deposition algorithms which remove material as the pollutants are transported downwind while maintaining a mass balance
- Treatment of chemical transformations
- Consideration of large-scale dispersion by inclusion of a three-dimensional wind field.

Although ASPEN addresses deposition and chemical transformations, it does not include consideration of large-scale dispersion. Application of these parameters at distances longer than 50 km is likely to result in a significant misrepresentation of the distribution of material within the modeled atmosphere.

However, comparison of observed data with model predictions, described in Attachment 5, showed some unexpected underpredictions, suggesting that medium-range transport (50 to 200 km) may have a significant impact on outdoor concentrations of some HAPs. Estimation of these contributions would require application of a regional model that addresses mesoscale air flow patterns.

EPA guidelines also caution against the use of urban dispersion parameters at downwind distances of less than 100 meters. Therefore, for this project the closest modeling receptors to the emission source were placed at 100 meters.

Building Wake Effects

Although ASPEN includes algorithms for evaluating building wake effects, they were not applied in this project due to lack of data pertaining to configuration of structures surrounding elevated point sources. Because building wake effects increase turbulence very near to the source, they generally result in higher ground-level concentrations in that vicinity than otherwise expected.

Uncertainties

The result of neglecting these effects is likely to be some underestimate of ground level ambient concentrations very close to elevated point sources. A recent study found that inclusion of building downwash increased maximum short-term average ground-level concentrations predicted by ISCST by a factor of 3 to 6 (Gratt and Levin, 1995). The effect of neglecting building downwash on long-term average concentrations resulting from multiple elevated and ground level sources at different locations, as modeled in this study, is likely to be considerably smaller, since this value is a composite of many contributions, only a few of which might be affected by downwash. The investigation of this issue in the sensitivity analysis, described in Attachment 4, suggests that a conservative estimate of the effect of omitting downwash would be an underestimate of tract average concentrations

resulting from elevated point sources by about 4 percent on average, with a maximum underestimate of about 19 percent.

Elevated Terrain

ASPEN does not treat the effect of terrain elevations on ground-level ambient concentration estimates, but implicitly assumes flat terrain throughout the modeling domain. Ground-level ambient concentrations in elevated terrain are expected to be higher than for identical elevated point source emissions in flat terrain, although the effects of terrain are generally less than the effects of building downwash or urban/rural designation (Gratt and Levin, 1995).

Uncertainties

The effect of neglecting terrain was investigated for this study in two ways. For the modeling sensitivity analysis described in Attachment 4, parallel ISCLT2 simulations with and without consideration of terrain elevations for the Greenpoint/Williamsburg test area showed that concentration estimates using the flat terrain assumption ranged from 5 percent lower to 3 percent higher than those made with terrain elevation specified. However, because the test area has very moderate terrain elevations ranging between 0 and approximately 10 meters, this result cannot be generalized to other areas that have more extreme terrain slopes. It is difficult to select a representative site for a test of the impact of terrain on exposure concentrations, since it depends not only on the terrain elevations in the area, but on the elevations where population activity takes place relative to the elevations of the emission source locations. A more general analysis of the impact of terrain is presented in Attachment 7. The results suggest that only a small fraction of outdoor concentrations in the vicinity of populations is likely to be significantly underestimated due to neglect of terrain elevation.

CONCLUSIONS

The dispersion and mapping modules of ASPEN used a number of simplifications to make the nationwide modeling of the large number of HAPs in this study feasible, while addressing the most significant dispersion factors. Our analyses suggest that these simplifications are not likely to have a large impact on the accuracy of long-term average concentrations estimates that are the focus of this study. We note, however, that some of these simplifications might have a more significant influence on the accuracy of short-term concentration estimates

6 MODELED CONCENTRATION ESTIMATES

The ASPEN dispersion and mapping modules were applied to the 48-state region using the national HAP emission inventory for 1990 described in Chapter 4 and the other input data described in Chapter 5. Each of the 10 emission categories was modeled individually. Background values, described below, are also included in the total modeled ambient concentrations as an eleventh source category. Results were obtained as 3-hour annual average concentrations, by source category, for the 60,000 census tracts in the modeling region. As discussed in Chapter 5, the concentration predictions are designed to approximate the population-weighted average concentration for each census tract.

BACKGROUND CONCENTRATIONS

The emissions inventory and modeling methodology described in the previous chapters are used to estimate long-term concentrations of HAPs attributable to 1990 anthropogenic emissions within a relatively short-range of the modeling receptor, i.e., 50 km. For many HAPs, however, current outdoor concentrations may include "background" components attributable to long-range transport, re-suspension of historical emissions, and non-anthropogenic sources. To accurately estimate 1990 outdoor concentrations of HAPs, it is necessary to account for these background concentrations which are not represented by atmospheric modeling of 1990 anthropogenic emissions.

In this study, background concentrations are represented by inclusion of concentration values measured at "clean air locations" remote from the impact of local anthropogenic sources. Background values were identified from the literature for 28 HAPs and are shown in Table 6-1. For these HAPs, the estimated concentration in each census tract is determined by summing together the background value, which is constant across all census tracts, and the modeled concentrations arising from current emissions.

As shown in the table, a variety of types of observations are used to estimate background concentrations for this study. When more than one type of information was identified, they were generally given priority as follows.

1. Mid-range of observations specified as background
2. Lower end of range specified as Northern Hemisphere average
3. Lower end of range specified as global average
4. Lower end range specified as remote/rural

Table 6-1 indicates that almost half of the HAPs with identified background concentrations have known or suspected natural sources of emissions. For example, carbon disulfide and methyl iodide are emitted in abundance from the activity of marine algae. For the others, concentrations at remote locations are due to persistence and long range transport.

For HAPs not listed in Table 6-1, either no background concentration values were identified in the technical literature, or the background value was determined to have a high likelihood of being zero (e.g., measured values frequently below the minimum detection level). In those cases background is implicitly assumed to be zero, which may result in underestimation of outdoor concentrations in some cases.

SUMMARY STATISTICS FOR MODELED AMBIENT CONCENTRATIONS

To provide annual average total concentrations, the results for the eight 3-hour time blocks were averaged and the concentrations attributed to each source category were summed. Table 6-2 summarizes the distributions among census tracts of annual average concentration predictions for each HAP.

Because each modeled concentration represents a census tract, and because the census tracts have roughly equal populations, the mean values are approximations of a national population-weighted mean concentration. The HAPs with the highest overall mean concentration predictions are as follows.

• toluene	3.8 $\mu\text{g}/\text{m}^3$
• xylene	2.8 $\mu\text{g}/\text{m}^3$
• methyl chloroform	2.8 $\mu\text{g}/\text{m}^3$
• benzene	2.0 $\mu\text{g}/\text{m}^3$
• formaldehyde	1.4 $\mu\text{g}/\text{m}^3$
• methyl chloride	1.3 $\mu\text{g}/\text{m}^3$
• carbonyl sulfide	1.2 $\mu\text{g}/\text{m}^3$
• hydrochloric acid	1.2 $\mu\text{g}/\text{m}^3$
• methanol	1.0 $\mu\text{g}/\text{m}^3$

For two of these HAPs the mean concentration predictions are dominated by background concentration assumptions: methyl chloride and carbonyl sulfide. For each of the other HAPs the mean concentration predictions are dominated by area and/or mobile source contributions, and are higher in urban areas¹.

Table 6-2 shows that, except for 4 HAPs with concentrations dominated by background assumptions, the mean concentrations are greater than the median concentrations for all HAPs, indicating that the predicted concentrations do not have normal distributions.

The range of predicted concentrations among census tracts is large for most HAPs. Sixty-six of the 148 HAPs (45%) have a median concentration prediction of 0.0 $\mu\text{g}/\text{m}^3$. With only one exception (dimethyl formamide), concentrations for all of these HAPs are dominated by point sources, and, therefore, are not widely dispersed. Of the other 82 HAPs, the ratios between the maximum and median concentration predictions range from 2.5 to 8×10^{10} with a median value of 167. For the 78 HAPs with nonzero 25th percentile values, the median interquartile range (the range between the 25th and 75th percentile of the modeled concentrations) spans a factor of 5.

¹ In this study an urban census tract was defined as one with a residential population density of greater than 750 people/km². See the discussion in Chapter 5 for more details.

Figure 6-1 presents graphical representations of the predicted concentrations ranges for 40 candidate priority HAPs² with box plots. In these box plots, the top and bottom of the box represent the 75th and 25th percentiles of the data and the line inside the box represents the median. The boundaries of the vertical lines mark the 5th and 95th percentile values.

Of the 40 candidate priority HAPs, concentration predictions for 5 are dominated³ by background concentration assumptions (carbon tetrachloride, chloroform, ethylene dibromide, mercury compounds, methyl chloride), 8 are dominated by point source contributions (acrylamide, coke oven emissions, hydrazine, methylene diphenyl diisocyanate, quinoline, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, vinylidene chloride), 6 are dominated by area source contributions (acrylonitrile, p-dichlorobenzene, 1,3-dichloropropene, ethyl acrylate, tetrachloroethylene, vinyl chloride), and 1 is dominated by mobile source contributions (1,3-butadiene). With one exception (1,1,2-trichloroethane) all the point source dominated HAPs of this group have concentration contributions exclusively from point sources.

As presented in Figure 6-1, the HAPs with the smallest spans are those dominated by background concentrations (interquartile ranges of less than a factor of 2). The one dominated by mobile sources has an interquartile range spanning a factor of approximately 6. The interquartile ranges for area source-dominated HAPs vary from factors of less than 10 (tetrachloroethylene, p-dichlorobenzene, 1,3-dichloropropene) to factors of approximately 500 (acrylonitrile, ethyl acrylate). As noted above, many of the point source-dominated HAPs have concentration estimates of 0.0 for more than half of the tracts (i.e., 0.0 median tract concentration).

In Attachment 8 statistical summaries similar to Table 6-2 are presented for the predicted concentrations of the 40 candidate priority HAPs for the tracts contained within each of the 10 most populous US metropolitan statistical areas (MSAs) and primary metropolitan statistical areas (PMSAs):

- Atlanta, GA
- Chicago, IL
- Dallas, TX
- Detroit, MI
- Houston, TX
- Los Angeles-Long Beach, CA
- Nassau-Suffolk, NY
- New York, NY
- Philadelphia, PA-NJ
- Washington DC, VA, MD

² Section 112(c)(3) of the Clean Air Act requires the US EPA to determine the 30 HAPs that present the greatest threat to public health, i.e., the 30 priority HAPs. On the basis of available toxicity, ambient air monitoring, and emissions inventory data, the EPA has identified a list of 40 candidate HAPs for the priority list. The list of 40 includes 38 of this study's 148 target HAPs, as well as coke oven emissions. In addition, it includes a group of 16 polycyclic aromatic hydrocarbons designated as "16-PAH". This group is equivalent to the combination of polycyclic organic compounds (POM) and naphthalene simulated in this study.

³ For this analysis if more than two-thirds of the mean predicted concentration for a HAP was contributed by a single source type, the HAP is characterized as being dominated by that source type.

Because of the large span of concentration predictions for many of these HAPs, there are some large discrepancies between MSA mean concentration predictions and the overall urban mean concentration predictions from Table 6-2. Table 6-3 presents a summary of discrepancies that exceed a factor of 3 ; i.e., the MSA mean concentration prediction is more than 3 times as high, or less than 0.33 as high, as the overall urban mean prediction. The table shows that Atlanta, Nassau-Suffolk, and Washington DC MSAs are predicted to have mean concentrations less than a third as high as the urban mean for 15, 10 and 12 of the 40 candidate priority HAPs, respectively, with the remainder of the HAP predictions within a factor of 3 of the overall urban mean. By contrast, Houston is predicted to have concentrations more than 3 times as high as the overall urban mean for 7 of the 40 candidate priority HAPs, and concentrations less than 0.33 times as high for only 3. The other MSAs show a mix of both high and low discrepancies.

Figures 6-2 through 6-9 present box plot representations of the predicted concentrations ranges for 8 of these HAPs, to compare the concentration distributions among each of the 10 MSAs and PMSAs, and with the distribution among all urban tracts. Figure 6-3, 6-4, and 6-6 show that the predicted concentration are very similar both within and among the metropolitan areas for benzene, chromium, and formaldehyde, respectively. The concentration predictions for all of these HAPs include significant contributions from point, area, and mobile source emissions. Benzene and formaldehyde also have background contributions, and formaldehyde has contributions from secondary formation as well. The predicted concentration distributions are somewhat more variable for acrylonitrile and ethylene oxide (Figures 6-2 and 6-5), which include contributions from a combination of point and area source emissions. Those HAPs with concentration contributions exclusively from point sources (hydrazine, methylene diphenyl diisocyanate, and quinoline) show the greatest variability in predicted concentration contributions both within and among the metropolitan areas.

PRIMARY AND SECONDARY CONCENTRATION CONTRIBUTIONS

The modeled concentrations of seven HAPs include contributions from secondary formation through atmospheric reactions. Secondary contributions were estimated as the difference between precursor species concentrations in inert (without reactive decay) and reactive simulations. Table 6-4 summarizes modeled primary and secondary contributions to total mean and maximum concentrations for these HAPs, as well as contributions from background assumptions for two HAPs: formaldehyde and phosgene. Because both of these HAPs have a significant contribution from modeled secondary formation, much of the background concentration is likely to be the result of secondary formation as well, but from sources more distant than 50 km, the downwind distance limitation of the simulations for this study. Table 6-4 also presents estimates from a previous photochemical modeling study with the UAM-Tox model (Ligocki et al., 1992), which included a much more detailed treatment of secondary formation.

As shown in the table, the average phosgene concentration is dominated by background assumptions. For the remaining HAPs, the contributions of primary emissions to the mean concentrations range from a high of 87 percent for methyl ethyl ketone to a low of 27 percent for propionaldehyde. For acetaldehyde and propionaldehyde secondary formation accounts for a majority of the simulated mean concentrations. For the others, the secondary contribution is smaller but not negligible. The primary contribution to acetaldehyde is within the range found in the UAM-Tox study, but the primary contribution for

formaldehyde is somewhat higher. This may be due to an underestimate of secondary concentrations in the ASPEN model: some precursor emissions may have been omitted; and/or significant secondary formation is likely to occur further than 50 km from sources, but would not be included in the ASPEN estimates. However, because the background concentration includes secondary formation from sources at greater distances, the downwind distance limitation should be offset to some extent. It is also possible that primary formaldehyde emissions are overestimated. This issue is discussed further in the model performance evaluation in Attachment 5.

The contribution to the maximum concentrations from primary emissions is nearly 100 percent for most of the HAPs. This is not surprising, since the maximum concentrations generally occur in the near vicinity of major point sources, where the highest concentration impacts of primary emissions occur, but insufficient time for chemical conversion has elapsed.

CONCENTRATION-TO-EMISSIONS RATIOS

Point, area, and mobile emission sources are likely to show some differences in their relative influence on air quality, due to differences in their spatial configurations. For example, point sources are often elevated so that their emissions are diluted by the time they reach ground level, resulting in lower concentrations than non-elevated emissions of equal magnitude. The locations of mobile source emissions are typically more dispersed than are point sources, so that they influence a greater fraction of the census tracts. The location patterns of some area sources, such as consumer solvents, are similar to mobile sources, while the location patterns of other area sources, such as small industrial sources, are more similar to point sources.

To investigate the potential impact of these differences, the source category contributions to the overall tract mean concentrations, shown in Table 6-2, were compared to the corresponding source category emissions for each HAP from Table 4-3. For each HAP/source category combination, the ratio of the mean tract concentration contribution to emissions was calculated. Omitting the 7 HAPs with secondary contributions, the median ratio across HAPs, is 0.50×10^{-3} for point sources (142 HAPs, including coke oven emissions), 1.24×10^{-3} for area sources (62 HAPs), and 0.89×10^{-3} for mobile sources (29 HAPs). A Kruskal-Wallis test shows all three medians to be significantly different at the 99% level of confidence. The respective coefficients of variation (standard deviation \div mean) are 0.69, 0.34, and 0.19, indicating the greatest variability in concentration/emissions ratios for point sources and the least variability for mobile sources. These findings reflect primarily the differences between elevated and non-elevated sources (lower average ratio for point sources), as well as differences in source location patterns (higher coefficient of variation for point sources). The higher median ratio for area sources compared to mobile sources may indicate that area sources are located in more densely populated places on average than mobile sources, which tend to be the most spatially dispersed. Because census tracts are designed to have roughly equal populations, the tracts will be smaller and closer together where the population density is higher, so that more tracts will be impacted by a given level of emissions in each tract.

In addition, the median anthropogenic tract concentration for each HAP (the median concentration less the background concentration) was compared to the total emissions. The results were then stratified by dominant source category, defined as more than two-thirds of

emissions from either point, area, or mobile sources. Omitting HAPs with secondary contributions, there were 95 HAPs dominated by point sources, 18 dominated by area sources, and 5 dominated by mobile sources. (The remainder had no dominant emissions source category.) The median ratios of the median anthropogenic tract concentrations to total emissions are 0.00, 3.6×10^{-4} , and 7.6×10^{-4} , for point, area, and mobile source-dominated HAPs, respectively. Again, a Kruskal-Wallis test shows all three medians to be significantly different at the 99% level of confidence. The corresponding coefficients of variation were 3.78, 0.83, and 0.06, respectively. These findings primarily reflect the differences in location patterns among source categories, discussed above, with mobile source locations the most dispersed and point source locations the least.

Table 6-1. Estimated background concentrations of 28 hazardous air pollutants

Pollutant	Background Concentration ($\mu\text{g}/\text{m}^3$)	Source of Value	Natural Sources
Benzene	0.48	midrange of N. hemisphere background: Singh et al. (1985)	Yes
Bis(2-ethylhexyl) phthalate	0.0014	midrange of remote ocean air: Howard (1989)	Possible
Bromoform	0.021	lower end of global range: WMO (1991)	Yes
Carbon disulfide	0.047	lower end of global range: Khalil and Rasmussen (1984)	Yes
Carbon tetrachloride	0.88	Atlantic value: Howard (1990)	No
Carbonyl sulfide	1.2	Global value & lower end of global range: Khalil and Rasmussen (1984) & WMO (1991)	Yes
Chlordane	9.9E-06	midrange of remote N. Pacific: Howard (1991)	No
Chloroform	0.083	N. hemisphere background: Howard (1990)	Yes
Dibutylphthalate	0.0010	N. Atlantic average: Howard (1989)	Possible
Dioxins/furans (toxicity equivalents)	1.5E-08	EPA (1994b)	No
Ethylene dibromide	0.0077	Global value: WMO (1991)	Possible
Ethylene dichloride	0.061	lower end of N. hemisphere baseline: Howard (1990)	No
Formaldehyde	0.25	Irish W. coast and German N. coast: Lowe et al. (1981) & Platt et al. (1979)	Yes
Hexachlorobenzene	9.3E-05	value for Eniwetak Atoll: Howard (1989)	No
Hexachlorobutadiene	0.0018	remote N. hemisphere: Howard (1989)	No

continued

Table 6-1 (concluded). Estimated background concentrations of 28 hazardous air pollutants

Pollutant	Background Concentration ($\mu\text{g}/\text{m}^3$)	Source of Value	Natural Sources
Hexachloroethane	0.0048	mean N. hemisphere background: Howard (1989)	No
Lindane	0.00025	Everglades National Park: Howard (1991)	No
Mercury compounds	0.0015	EPA (1995a)	Yes
Methyl bromide	0.039	lower end of global range: WMO (1991)	Yes
Methyl chloride	1.2	mean global remote & global value: Howard (1989) & WMO (1991)	Yes
Methyl chloroform	1.1	N. hemisphere baseline: Howard (1990)	No
Methyl iodide	0.012	Global background: Howard (1993)	Yes
Methylene chloride	0.15	N. hemisphere background: Howard (1990)	No
Phosgene	0.061	rural, remote: Grosjean (1991a)	No
Polychlorinated biphenyls	0.00038	Bermuda annual average: Panshin and Hites (1994a)	No
Tetrachloroethylene	0.14	mean remote N. hemisphere (non-tropical): Wiedmann et al. (1994)	No
Trichloroethylene	0.081	lower end of N. hemisphere average: Howard (1990)	No
Xylene	0.17	N. hemisphere background: Howard (1990)	Yes

TABLE 6-2. Summary of ASPEN predicted concentrations ($\mu\text{g}/\text{m}^3$) for all census tracts.

TABLE 0-2. Summary of AQS EN predicted concentrations (µg/m ³) for air census tracts.												
HAP	Minimum	Percentiles				Maximum	Overall		Urban*		Overall Mean by Source	
		25 th	50 th	75 th	95 th		Mean	Point	Mean	Point	Area	Mobile
Acetaldehyde	0	0.23	0.50	1.0	2.1	21	0.71	0.96	0.58	0.22	0.43	
Acetamide	0	0	0	0	0	6.6e-6	5.1e-10	3.1e-10	5.1e-10			
Acetonitrile	0	0	6.1e-11	2.1e-5	2.8e-3	1.8	1.5e-3	2.1e-3	1.5e-3			
Acetophenone	0	0	0	0	1.2e-8	4.5e-4	1.1e-7	1.2e-7	1.1e-7			
Acrolein	0	0.062	0.14	0.27	0.72	20	0.23	0.30	6.3e-3	0.11	0.11	
Acrylamide	0	0	0	1.1e-7	8.3e-6	0.044	1.1e-5	1.5e-5	1.1e-5			
Acrylic acid	0	0	0	6.1e-5	1.3e-3	0.50	5.0e-4	6.6e-4	5.0e-4			
Acrylonitrile	0	1.9e-5	1.2e-3	0.010	0.058	7.7	0.014	0.020	3.8e-3	0.010		
Allyl chloride	0	0	0	0	7.7e-5	0.56	1.7e-4	2.1e-4	1.7e-4			
Aniline	0	0	1.1e-9	7.4e-5	2.3e-3	4.0	1.1e-3	1.4e-3	1.2e-3			
Anisidine	0	0	0	0	0	2.7e-3	4.9e-7	6.0e-7	4.9e-7			
Antimony	0	4.0e-5	1.5e-4	4.2e-4	1.7e-3	0.12	4.2e-4	6.1e-4	2.0e-4	1.9e-4	3.2e-5	
Arsenic	0	9.0e-5	2.2e-4	4.5e-4	1.3e-3	0.26	4.3e-4	5.7e-4	1.6e-4	1.5e-4	1.2e-4	
Benzene	0.48	0.90	1.6	2.7	5.0	79	2.0	2.7	0.10	0.43	1.0	
Benzotrichloride	0	0	0	0	0	0.020	8.5e-6	1.2e-5	8.5e-6			
Benzyl chloride	0	0	0	0	2.1e-4	0.26	1.4e-4	1.7e-4	1.4e-4			
Beryllium	0	2.1e-6	6.7e-6	1.7e-5	5.4e-5	2.2e-3	1.6e-5	2.0e-5	8.5e-6	6.4e-6	6.5e-7	
Biphenyl	0	8.9e-8	1.1e-6	1.0e-4	3.1e-3	1.3	9.7e-4	1.1e-3	9.7e-4	1.2e-6		
Bis(2-ethylhexyl) phthalate	1.4e-3	1.4e-3	1.4e-3	1.6e-3	4.7e-3	1.0	2.4e-3	2.8e-3	1.0e-3			
Bis(chloromethyl) ether	0	0	0	0	0	1.5e-3	2.3e-7	2.4e-7	2.3e-7			
Bromoform	0.021	0.021	0.021	0.023	0.031	1.1	0.024	0.024	3.6e-5	2.8e-3		
1,3-Butadiene	0	0.034	0.10	0.20	0.43	6.7	0.15	0.20	2.8e-3	0.033	0.11	
Cadmium	0	5.0e-5	1.5e-4	3.6e-4	9.9e-4	0.26	3.0e-4	3.7e-4	9.9e-5	2.0e-4	2.3e-6	
Calcium cyanamide	0	0	0	0	0	0.026	5.6e-6	6.5e-6	5.6e-6			
Captan	0	0	0	0	0	0.12	8.0e-6	2.5e-6	8.0e-6			
Carbaryl	0	0	0	0	8.2e-6	0.017	7.2e-6	8.0e-6	7.2e-6			
Carbon disulfide	0.047	0.047	0.048	0.054	0.13	58	0.085	0.087	0.034	4.4e-3		
Carbon tetrachloride	0.88	0.88	0.88	0.89	0.92	4.8	0.89	0.89	1.7e-3	8.4e-3		
Carbonyl sulfide	1.2	1.2	1.2	1.2	1.2	28	1.2	1.2	5.8e-3	1.5e-3		
Catechol	0	0	0	0	3.6e-7	0.15	5.4e-5	8.5e-5	5.4e-5			
Chloramben	0	0	0	0	0	1.4e-5	1.5e-9	8.6e-10	1.5e-9			
Chlordane	9.9e-6	9.9e-6	9.9e-6	9.9e-6	9.9e-6	0.042	1.6e-5	1.9e-5	5.7e-6			

Continued

TABLE 6-2 (continued). Summary of ASPEN predicted concentrations ($\mu\text{g}/\text{m}^3$) for all census tracts.

HAP	Percentiles						Overall Mean	Urban*		Overall Mean by Source		
	Minimum	25 th	50 th	75 th	95 th	Maximum		Mean	Point	Area	Mobile	
Chloroacetic acid	0	0	0	0	3.1e-5	0.15	2.6e-5	3.6e-5	2.6e-5			
Chlorobenzene	0	8.7e-3	0.030	0.077	0.24	38	0.071	0.10	8.8e-3	0.062		
Chloroform	0.083	0.084	0.087	0.095	0.16	8.8	0.11	0.11	8.5e-3	0.014		
Chloromethyl methyl ether	0	0	0	0	0	0.014	2.1e-6	2.2e-6	2.2e-6			
Chloroprene	0	1.5e-5	1.3e-3	0.012	0.080	12	0.018	0.026	2.9e-3	0.016		
Chromium	0	2.0e-4	5.8e-4	1.4e-3	4.3e-3	1.0	1.4e-3	1.9e-3	8.8e-4	3.3e-4	1.7e-4	
Cobalt	0	3.8e-5	1.1e-4	2.8e-4	8.0e-4	0.020	2.3e-4	3.1e-4	8.5e-5	1.3e-4	1.1e-5	
Cresol	0	0.021	0.054	0.10	0.18	1.7	0.070	0.096	2.8e-3	0.020	0.046	
Cumene	0	0.010	0.021	0.035	0.073	8.6	0.032	0.044	8.5e-3	0.010	0.014	
Cyanide compounds	0	0.020	0.060	0.13	0.24	0.85	0.083	0.12	7.2e-4		0.083	
2,4-D, salts and esters	0	0	0	0	1.1e-5	0.032	1.5e-5	2.1e-5	1.5e-5			
Dibutylphthalate	1.0e-3	1.1e-3	1.5e-3	1.9e-3	3.8e-3	0.13	1.8e-3	2.1e-3	1.5e-4	6.3e-4		
p-Dichlorobenzene	0	0.018	0.055	0.12	0.38	28	0.11	0.15	2.8e-3	0.10		
3,3'-Dichlorobenzidine	0	0	0	0	3.0e-7	7.3e-4	8.3e-7	1.2e-6	8.4e-7			
Dichloroethyl ether	0	0	0	0	1.5e-9	0.025	4.8e-6	7.0e-6	4.8e-6			
1,3-Dichloropropene	0	0.011	0.036	0.072	0.20	1.1	0.056	0.083	3.2e-5	0.056		
Dichlorvos	0	0	0	0	6.6e-8	7.3e-4	4.8e-7	6.7e-7	4.8e-7			
Diethanolamine	0	0	0	0	2.6e-4	0.092	8.5e-5	1.2e-4	8.5e-5			
N,N-Diethyl/dimethylaniline	0	0	0	0	6.3e-5	0.12	6.4e-5	9.1e-5	6.4e-5			
Diethyl sulfate	0	0	0	0	8.6e-5	0.016	1.4e-5	2.0e-5	1.4e-5			
3,3'-Dimethoxybenzidine	0	0	0	0	2.7e-8	3.0e-5	7.3e-9	1.0e-8	7.3e-9			
Dimethyl formamide	0	0	0	0	8.8e-6	5.0	3.7e-3	4.5e-3	7.4e-6	3.7e-3		
1,1-Dimethyl hydrazine	0	0	0	0	0	4.5e-3	5.5e-7	8.3e-7	5.5e-7			
Dimethyl phthalate	0	0	0	0	5.6e-7	0.49	2.7e-4	2.4e-4	2.7e-4			
Dimethyl sulfate	0	0	0	0	8.3e-5	0.044	2.1e-5	3.0e-5	2.1e-5			
4,6-Dinitro-o-cresol	0	0	0	0	0	1.8e-3	2.0e-6	2.7e-6	2.0e-6			
2,4-Dinitrophenol	0	0	0	0	5.4e-7	3.4e-3	1.6e-5	2.1e-5	1.6e-5			
2,4-Dinitrotoluene	0	0	0	0	1.4e-7	0.062	2.9e-5	2.5e-5	2.9e-5			
1,4-Dioxane	0	0	0	0	2.6e-5	0.75	5.9e-4	7.8e-4	5.9e-4			
Epichlorohydrin	0	0	0	0	9.5e-6	0.41	4.5e-4	5.9e-4	4.5e-4			
1,2-Epoxybutane	0	0	0	0	7.0e-5	0.19	4.2e-5	5.2e-5	4.2e-5			

Continued

TABLE 6-2 (continued). Summary of ASPEN predicted concentrations ($\mu\text{g}/\text{m}^3$) for all census tracts.

TABLE 6-2 (continued). Summary of ASPEN predicted concentrations (µg/m³) for all census tracts.												
HAP	Percentiles						Maximum	Overall Mean	Urban		Overall Mean by Source	
	Minimum	25 th	50 th	75 th	95 th	Mean			Point	Area	Mobile	
Ethyl acrylate	0	7.8e-6	5.5e-4	4.4e-3	0.027	4.4	6.4e-3	9.1e-3	7.0e-4	5.7e-3		
Ethyl carbamate	0	0	0	0	1.6e-5	0.010	4.1e-6	5.8e-6	4.1e-6			
Ethyl chloride	0	2.1e-4	1.8e-3	0.013	7.8e-2	10	0.018	0.025	3.3e-3	0.015		
Ethylbenzene	0	0.10	0.30	0.57	1.0	9.0	0.40	0.55	0.024	0.033	0.33	
Ethylene dibromide	7.7e-3	7.7e-3	7.7e-3	7.7e-3	8.9e-3	1.2	8.1e-3	8.2e-3	4.3e-4			
Ethylene dichloride	0.061	0.061	0.064	0.089	0.23	22	0.10	0.11	7.9e-3	0.031		
Ethylene glycol	0	0.089	0.28	0.51	1.3	38	0.39	0.57	0.013	0.38		
Ethylene oxide	0	4.3e-4	1.5e-3	4.1e-3	0.019	1.9	5.4e-3	7.6e-3	3.4e-3	2.0e-3		
Ethylene thiourea	0	0	0	0	4.5e-8	1.2e-3	1.9e-7	3.0e-7	1.9e-7			
Ethylidene dichloride	0	0	0	0	0	5.0e-5	2.4e-8	2.6e-8	2.4e-8			
Formaldehyde	0.25	0.58	1.0	1.7	4.0	51	1.4	1.9	0.082	0.37	0.74	
Glycol ethers	0	0.12	0.37	0.80	2.0	24	0.62	0.90	0.051	0.57		
Heptachlor	0	0	0	0	0	0.061	1.9e-5	1.5e-5	1.9e-5			
Hexachlorobenzene	9.3e-5	9.3e-5	9.3e-5	9.3e-5	9.3e-5	0.058	1.3e-4	1.5e-4	4.0e-5			
Hexachlorobutadiene	1.8e-3	1.8e-3	1.8e-3	1.8e-3	1.8e-3	7.0e-3	1.8e-3	1.8e-3	3.1e-6			
Hexachlorocyclopentadiene	0	0	0	0	0	0.79	1.1e-4	1.7e-4	1.1e-4			
Hexachloroethane	4.8e-3	4.8e-3	4.8e-3	4.8e-3	4.9e-3	0.044	4.9e-3	4.9e-3	2.8e-5			
Hexane	0	0.19	0.50	0.95	2.2	72	0.76	1.1	0.11	0.41	0.23	
Hydrazine	0	0	0	7.9e-9	3.2e-5	0.032	1.3e-5	1.8e-5	1.3e-5			
Hydrochloric acid	0	0.15	0.58	1.6	3.9	300	1.2	1.7	0.21	0.94	5.8e-3	
Hydrofluoric acid	0	2.4e-3	9.5e-3	0.022	0.055	2.2	0.017	0.024	6.9e-3	0.010	1.9e-4	
Hydroquinone	0	0	0	9.2e-8	2.0e-5	0.038	1.0e-5	1.5e-5	1.0e-5			
Lead	0	1.5e-3	3.7e-3	7.7e-3	0.018	5.5	6.6e-3	8.9e-3	2.2e-3	2.7e-3	1.6e-3	
Lindane	2.5e-4	2.5e-4	2.5e-4	2.5e-4	2.5e-4	7.2e-3	2.5e-4	2.5e-4	1.1e-6			
Maleic anhydride	0	4.3e-6	2.9e-4	2.4e-3	0.016	2.4	3.7e-3	5.2e-3	6.4e-4	3.1e-3		
Manganese	0	1.4e-3	3.2e-3	6.2e-3	0.016	0.82	5.4e-3	7.2e-3	1.6e-3	2.8e-3	1.0e-3	
Mercury compounds	1.5e-3	1.6e-3	1.7e-3	2.0e-3	3.4e-3	0.022	2.0e-3	2.2e-3	1.8e-4	2.5e-4	3.3e-5	
Methanol	0	0.24	0.67	1.3	3.2	62	1.0	1.4	0.15	0.79	0.034	
Methoxychlor	0	0	0	0	1.4e-8	8.7e-3	6.6e-7	7.4e-7	6.6e-7			
Methyl bromide	0.039	0.039	0.039	0.039	0.043	1.5	0.041	0.042	2.1e-3			
Methyl chloroform	1.1	1.4	2.2	3.3	6.6	87	2.8	3.5	0.24	1.4		
Methyl chloride	1.2	1.2	1.2	1.3	1.3	7.9	1.3	1.3	7.5e-3	7.7e-3		

Continued

TABLE 6-2 (continued). Summary of ASPEN predicted concentrations ($\mu\text{g}/\text{m}^3$) for all census tracts.

HAP	Percentiles							Overall Mean by Source			
	Minimum	25 th	50 th	75 th	95 th	Maximum	Overall Mean	Urban Mean	Point	Area	Mobile
Methyl ethyl ketone	0	0.19	0.53	1.1	2.7	87	0.85	1.2	0.15	0.64	0.061
Methyl hydrazine	0	0	0	3.0e-10	3.9e-7	6.0e-3	1.1e-6	1.1e-6	1.1e-6		
Methyl iodide	0.012	0.012	0.012	0.012	0.012	0.14	0.012	0.012	3.0e-5		
Methyl isobutyl ketone	0	0.029	0.10	0.25	0.71	9.9	0.20	0.28	0.030	0.17	
Methyl isocyanate	0	0	0	0	0	0.11	1.6e-5	1.2e-5	1.6e-5		
Methyl methacrylate	0	3.4e-6	3.0e-4	3.3e-3	0.020	37	6.7e-3	8.8e-3	3.7e-3	3.0e-3	
Methyl tert-butyl ether	0	0.085	0.26	0.54	1.3	40	0.40	0.58	0.032	0.087	0.28
4,4'-methylene bis(2-chloroaniline)	0	0	0	0	2.4e-8	7.9e-3	5.4e-7	8.4e-7	5.4e-7		
Methylene chloride	0.15	0.20	0.30	0.49	1.1	51	0.45	0.56	0.10	0.20	
Methylene diphenyl diisocyanate	0	0	5.9e-6	1.0e-4	1.6e-3	2.3	7.0e-4	9.5e-4	7.0e-4		
4,4'-Methylenedianiline	0	0	0	0	1.0e-5	0.015	9.8e-6	1.2e-5	9.8e-6		
Naphthalene	0	0.039	0.11	0.21	0.41	3.9	0.15	0.21	5.9e-3	0.026	0.11
Nickel	0	8.6e-4	2.6e-3	6.8e-3	0.029	0.78	6.9e-3	1.0e-2	2.4e-3	3.8e-3	7.9e-4
Nitrobenzene	0	0	0	3.0e-8	1.7e-4	0.26	1.4e-4	1.7e-4	1.4e-4		
4-Nitrophenol	0	0	0	0	0	0.034	1.6e-5	2.3e-5	1.6e-5		
2-Nitropropane	0	0	0	0	3.1e-4	0.040	6.0e-5	8.2e-5	6.0e-5		
Parathion	0	0	0	0	0	6.6e-3	3.2e-7	4.6e-7	3.2e-7		
PCDD/PCDFs	1.5e-8	1.5e-8	1.7e-8	2.0e-8	6.4e-8	2.2e-6	2.5e-8	3.0e-8	7.5e-9	2.1e-9	3.0e-10
Pentachloronitrobenzene	0	0	0	0	0	1.9e-3	1.4e-7	1.1e-7	1.4e-7		
Pentachlorophenol	0	0	0	0	5.0e-6	0.014	6.2e-6	6.2e-6	6.3e-6		
Phenol	0	0.039	0.092	0.17	0.32	38	0.13	0.17	0.012	0.053	0.058
Phosgene	0.061	0.062	0.064	0.068	7.4e-2	0.16	0.066	0.067	1.3e-3	3.6e-3	
Phthalic anhydride	0	1.1e-4	1.2e-3	8.9e-3	0.048	7.4	0.012	0.017	1.6e-3	0.010	
Polychlorinated biphenyls	3.8e-4	3.8e-4	3.8e-4	3.8e-4	4.2e-4	0.015	4.0e-4	4.0e-4	1.9e-5	2.7e-7	
Polycyclic organic matter	0	0.062	0.18	0.35	0.92	10	0.27	0.39	0.069	0.064	0.14
P-phenylenediamine	0	0	0	0	4.3e-8	1.4e-3	4.4e-7	5.9e-7	4.4e-7		
Propionaldehyde	0	0.048	0.11	0.21	0.44	4.0	0.15	0.21	0.015	0.041	0.097
Propoxur	0	0	0	0	0	4.8e-5	1.8e-8	2.6e-8	1.8e-8		
Propylene dichloride	0	1.0e-6	7.8e-5	6.8e-4	5.0e-3	3.4	1.8e-3	2.7e-3	9.6e-4	8.8e-4	
Propylene oxide	0	4.9e-7	3.2e-5	5.1e-4	9.0e-3	1.3	2.1e-3	2.9e-3	1.9e-3	2.1e-4	
1,2-Propylenimine	0	y 0	0	0	3.7e-6	6.7e-3	1.0e-6	1.6e-6	1.0e-6		

Continued

TABLE 6-2 (concluded). Summary of ASPEN predicted concentrations ($\mu\text{g}/\text{m}^3$) for all census tracts.

TABLE 6-2 (continued): Summary of AQS EN predicted concentrations (pg/m ³) for air census tracts.												
HAP	Percentiles					Maximum	Overall		Urban ^a		Overall Mean by Source	
	Minimum	25 th	50 th	75 th	95 th		Mean	Point	Mean	Point	Area	Mobile
Quinoline	0	0	0	0	8.2e-5	0.034	1.6e-5	2.3e-5	1.6e-5			
Quinone	0	0	0	0	1.8e-11	8.1e-3	6.6e-7	9.3e-7	6.6e-7			
Selenium	0	9.3e-5	3.2e-4	8.3e-4	2.4e-3	0.56	7.6e-4	1.1e-3	3.4e-4	4.1e-4	9.7e-6	
Styrene	0	0.010	0.042	0.097	0.25	31	0.082	0.12	0.016	0.028	0.039	
Styrene oxide	0	0	0	0	9.0e-6	3.8e-3	3.6e-6	4.9e-6	3.6e-6			
1,1,2,2-Tetrachloroethane	0	0	0	0	9.5e-6	0.076	4.2e-5	5.4e-5	4.2e-5			
Tetrachloroethylene	0.14	0.22	0.43	0.79	1.5	39	0.59	0.80	0.051	0.40		
Toluene	0	0.93	2.8	5.3	11	89	3.8	5.3	0.36	1.4	2.0	
2,4-Toluene diamine	0	0	0	0	1.6e-8	0.014	7.0e-7	6.8e-7	7.1e-7			
2,4-Toluene diisocyanate	0	0	3.1e-12	2.1e-5	2.5e-4	0.26	1.7e-4	2.0e-4	1.7e-4			
O-Toluidine	0	0	0	0	1.0e-6	7.6e-3	2.9e-6	4.1e-6	2.9e-6			
1,2,4-Trichlorobenzene	0	0	0	4.4e-6	8.3e-4	0.35	4.9e-4	6.0e-4	4.9e-4			
1,1,2-Trichloroethane	0	7.2e-5	2.2e-4	4.1e-4	2.3e-3	4.3	1.2e-3	1.7e-3	9.9e-4	2.2e-4		
Trichloroethylene	0.081	0.13	0.24	0.45	1.1	32	0.37	0.50	0.049	0.24		
2,4,6-Trichlorophenol	0	0	0	0	0	3.9e-4	6.8e-8	6.9e-8	6.8e-8			
Trifluralin	0	0	0	0	3.4e-8	0.041	5.5e-6	7.8e-6	5.5e-6			
2,2,4-Trimethylpentane	0	0.20	0.60	1.3	2.3	23	0.83	1.2	0.036	0.054	0.74	
Vinyl acetate	0	3.7e-5	2.5e-3	0.020	0.13	20	0.031	0.043	5.0e-3	0.026		
Vinyl bromide	0	0	0	0	0	8.5e-3	1.0e-6	8.3e-7	1.1e-6			
Vinyl chloride	0	5.6e-4	3.9e-3	0.020	0.098	13	0.024	0.034	4.4e-3	0.020		
Vinylidene chloride	0	0	0	3.4e-6	5.7e-5	0.51	2.0e-4	2.4e-4	2.00e-4			
Xylene	0.17	0.82	2.1	3.9	7.8	72	2.8	4.0	0.20	1.2	1.3	
Coke oven emissions	0	0	0	0	0.27	95	0.058	0.086	0.058			

^{*} Census tracts with residential population density greater than 750 persons/km².

Table 6-3. MSA mean concentration predictions for 40 candidate priority HAPs that differ from overall urban mean concentration predictions by more than a factor of 3¹.

HAP	Metropolitan Statistical Area									
	Atlanta	Chicago	Dallas	Detroit	Houston	Los Angeles	Nassau-Suffolk	New York	Philadelphia	Wash, DC
Acetaldehyde										
Acrolein										
Acrylamide	-	-	-	-	-	-	-	-		
Acrylonitrile	-	-	-	-	+				+	-
Arsenic										
Benzene										
Beryllium	-	-								
Bis(2-ethylhexyl) phthalate				+						
1,3-butadiene										
Cadmium	-									
Carbon tetrachloride										
Chloroform										
Chromium										-
Coke Oven	-	+	-	+	-	-	-	-	-	-
p-Dichlorobenzene										
1,3-dichloropropene										
Ethyl acrylate	-		-		+				+	-
Ethylene dibromide										
Ethylene dichloride					+	+				
Ethylene oxide			-							
Formaldehyde										
Hydrazine	-	-	-	-	+		-	-	-	-
Lead			+							
Manganese										
Mercury compounds										
Methyl chloride										
Methylene chloride										
Methylene diphenyl diisocyanate	-	-	-	-		+	-	-	-	-
Nickel	-							+		
16-PAH										
PCDD/PCDFs									+	
Propylene dichloride	-	-	-	-		-	-			-
Quinoline	-	+	-	+	+	-	-	-	-	-
Styrene										
1,1,2,2-tetrachloroethane	-	-	-	-	-	-	-	-	-	-
Tetrachloroethylene										
1,1,2-trichloroethane	-		-			-	-	-	-	-
Trichloroethylene										
Vinyl chloride	-		-		+				+	-
Vinylidene chloride	-		-	-	+	-	-	-	-	-

¹ "+": (MSA mean prediction) > 3 × (overall urban mean prediction). "-": (MSA mean prediction) < 0.33 × (overall urban mean prediction).

Table 6-4. Primary and secondary contributions to concentrations of seven HAPs.

HAP	UAM-Tox [*] primary	Contribution to Mean Concentration (%)			Contribution to Maximum Concentration (%)		
		primary	secondary	backgrd	primary	secondary	backgrd
acetaldehyde	10%-60%	40	60	0	96	4	0
acrolein	NA	75	25	0	99	1	0
cresol	NA	73	27	0	99	1	0
formaldehyde	20%-70%	71	12	17	97	2	0
methyl ethyl ketone	NA	87	13	0	100	0	0
phosgene	NA	0	7	93	0	62	38
propionaldehyde	NA	27	73	0	97	3	0

^{*} Findings from Ligocki et al. (1992) modeling study. The lower value is for summer; the higher value is for winter.

Figure 6-1
Distributions among census tracts of concentration predictions of selected HAPs

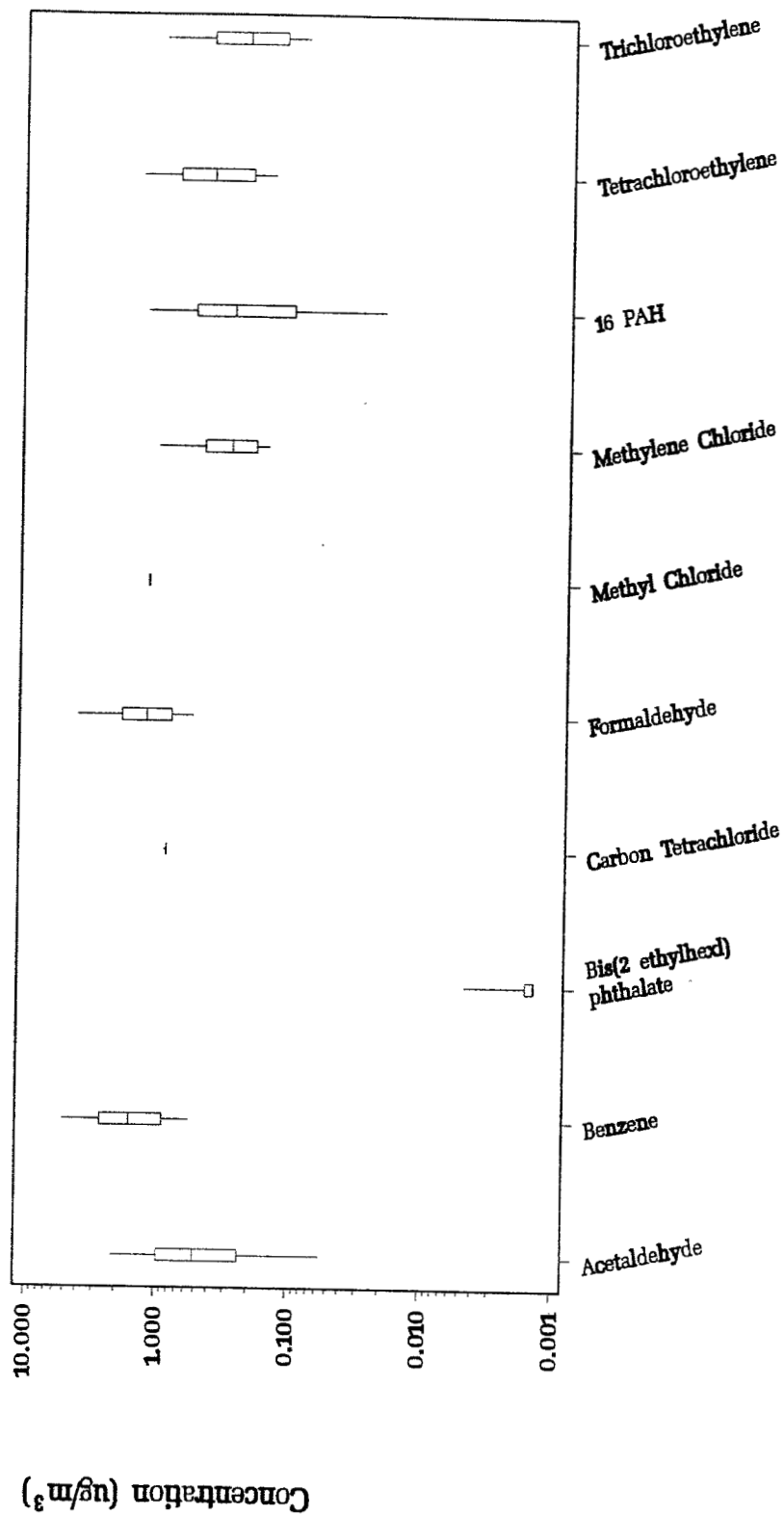


Figure 6-1 (continued)
Distributions among census tracts of concentration predictions of selected HAPs

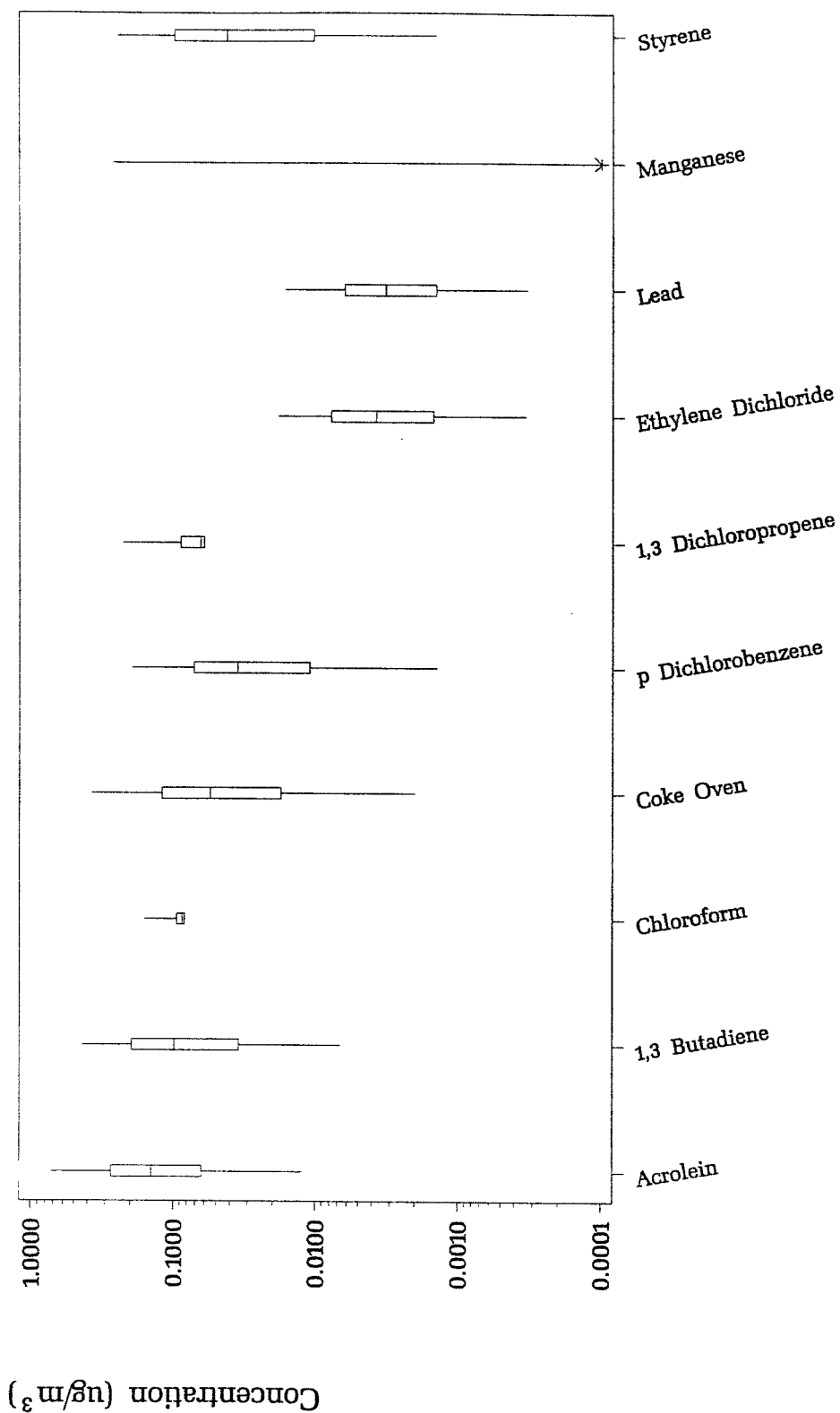


Figure 6-1 (continued)
Distributions among census tracts of concentration predictions of selected HAPs

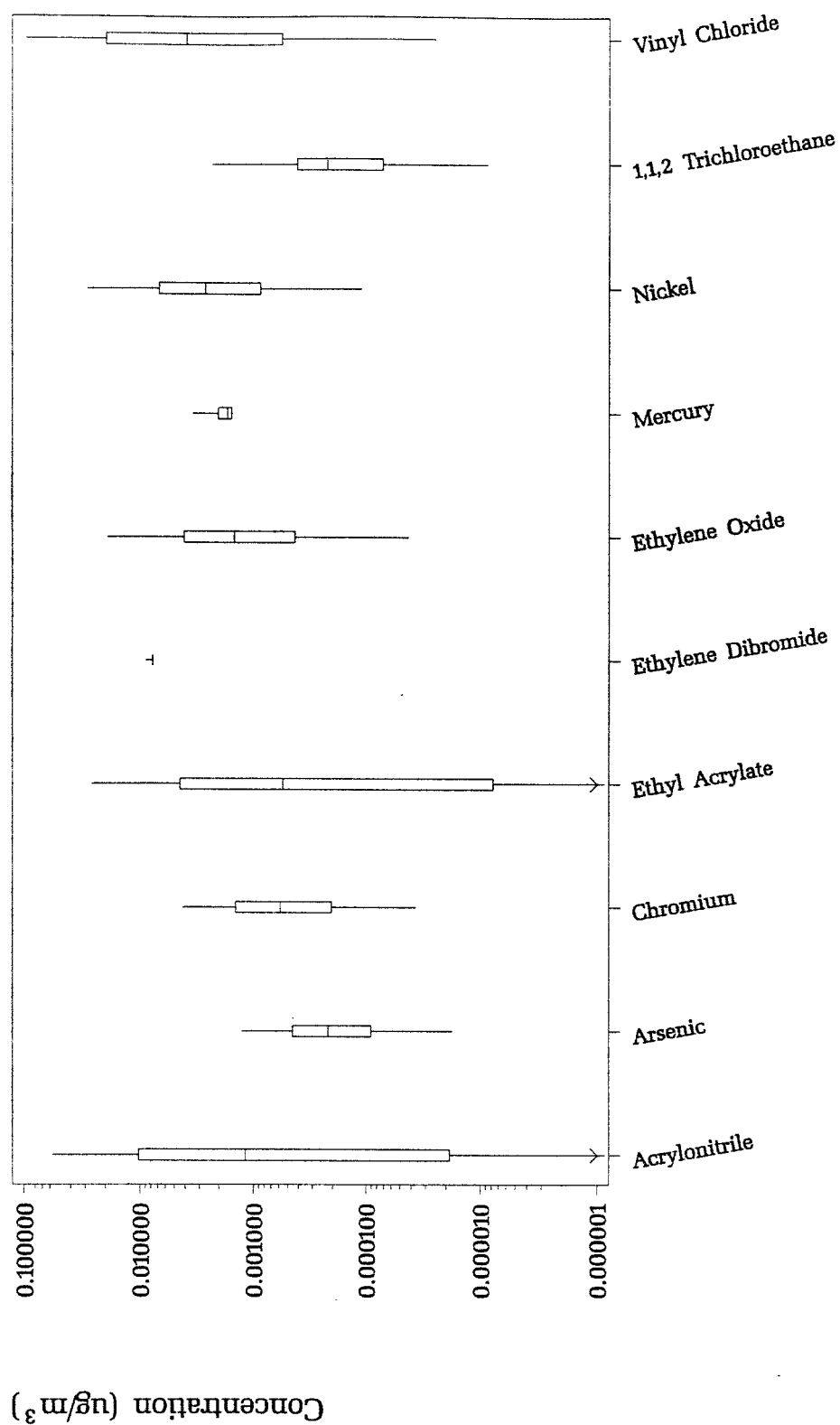


Figure 6-1 (concluded)
Distributions among census tracts of concentration predictions of selected HAPs

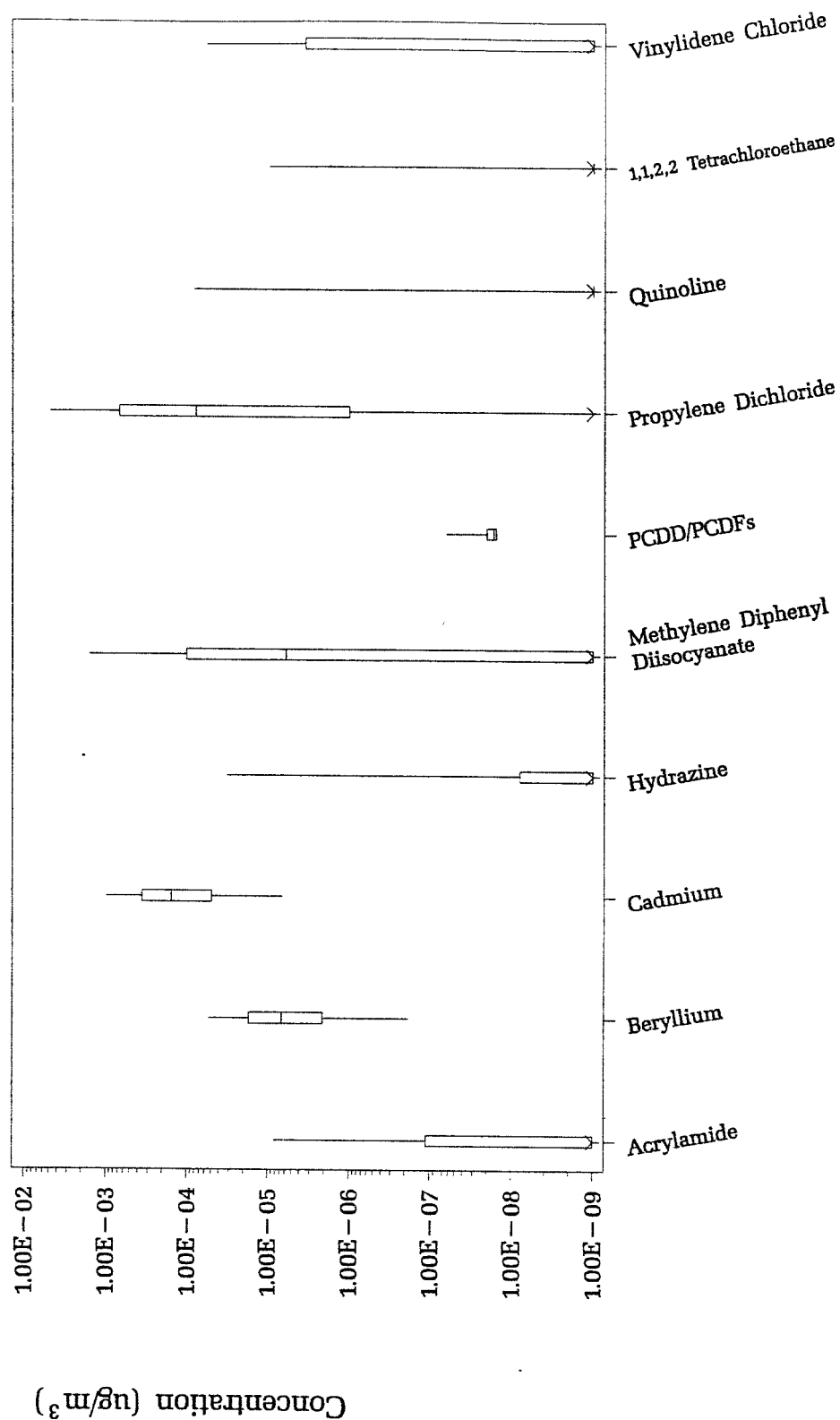


Figure 6-2

Distributions of Predicted Acrylonitrile Concentrations
Among Census Tracts

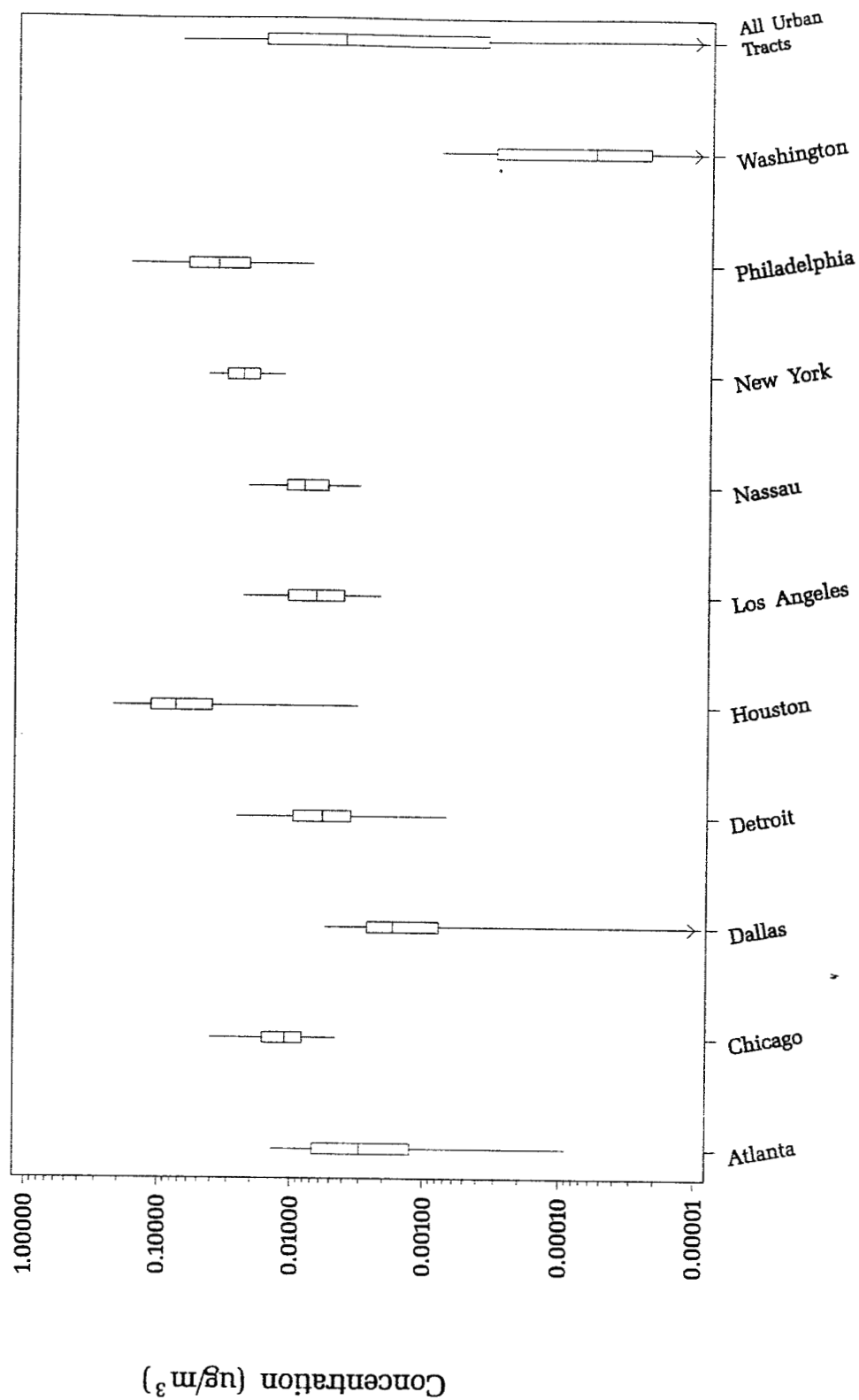


Figure 6-3
Distributions of Predicted Benzene Concentrations
Among Census Tracts

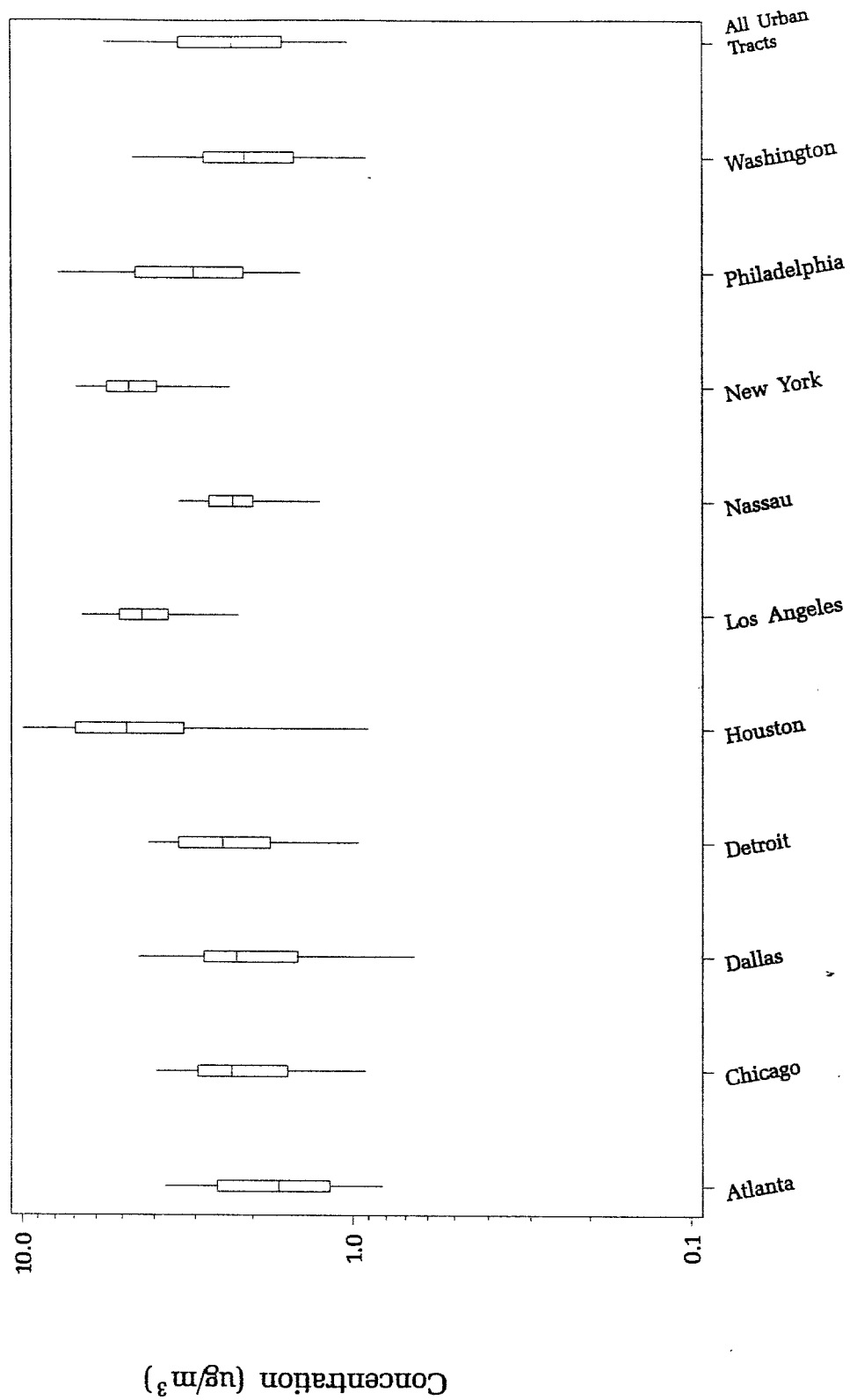


Figure 6-4
Distributions of Predicted Chromium Concentrations
Among Census Tracts

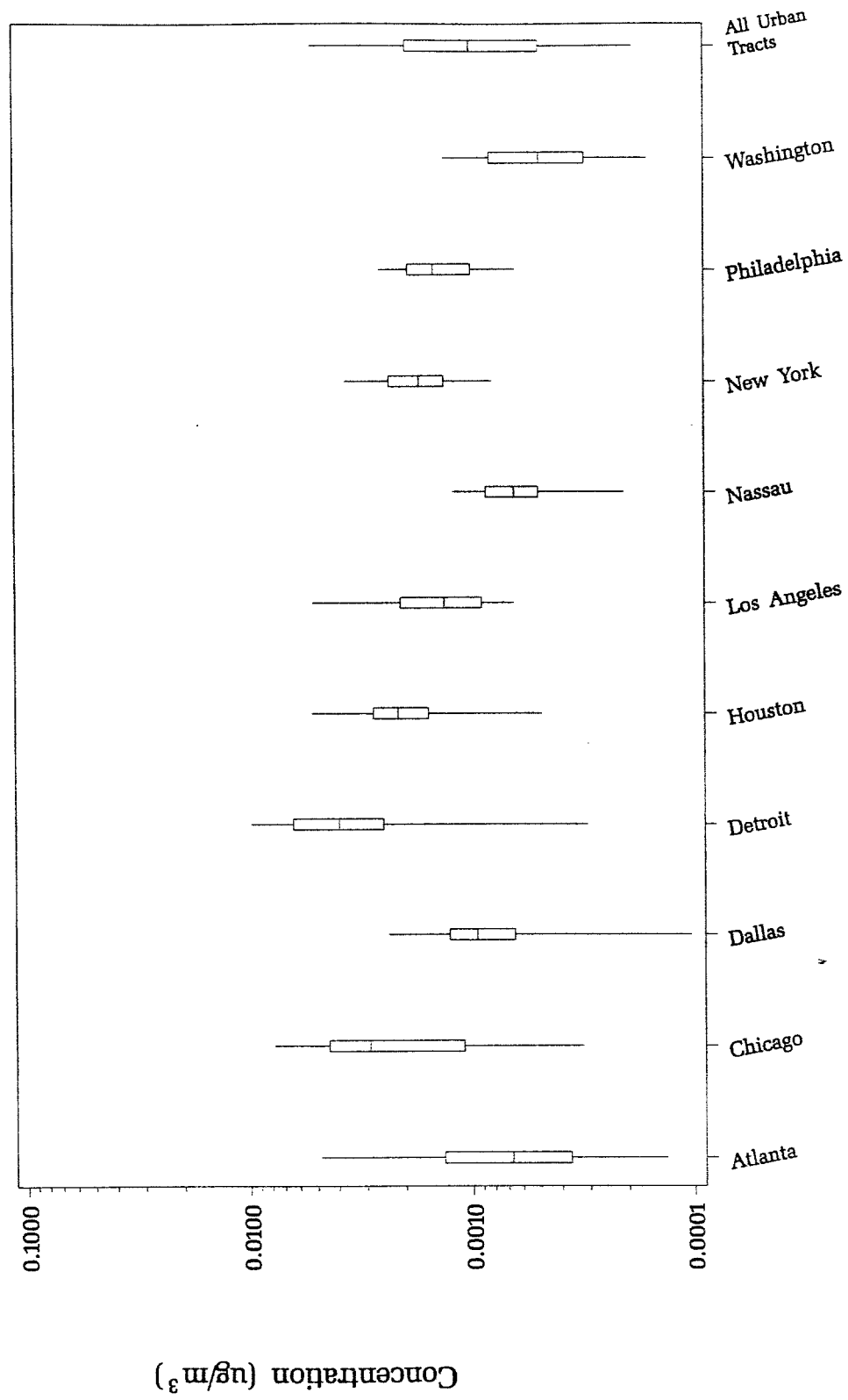


Figure 6-5
Distributions of Predicted Ethylene Oxide Concentrations
Among Census Tracts

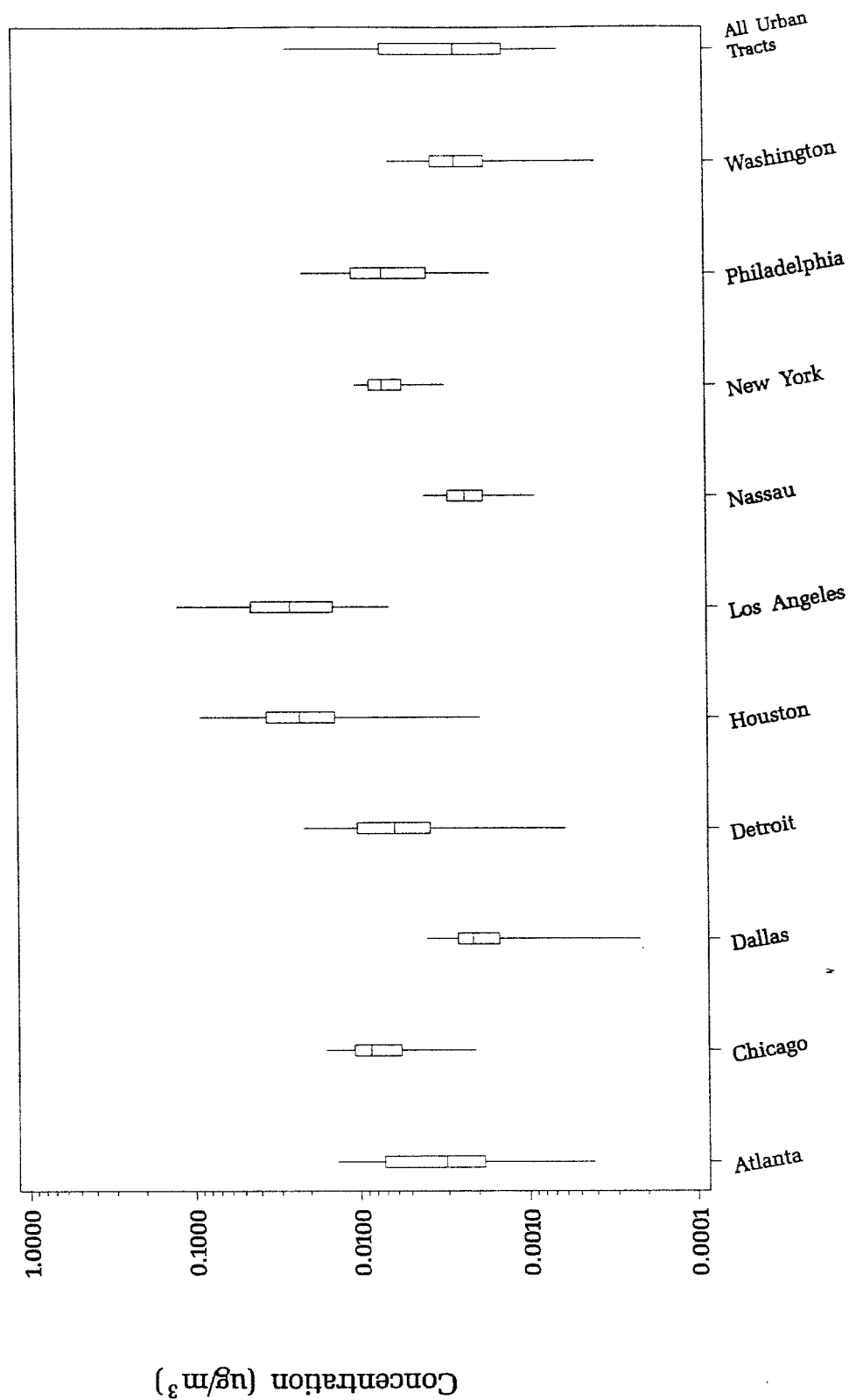


Figure 6-6
Distributions of Predicted Formaldehyde Concentrations
Among Census Tracts

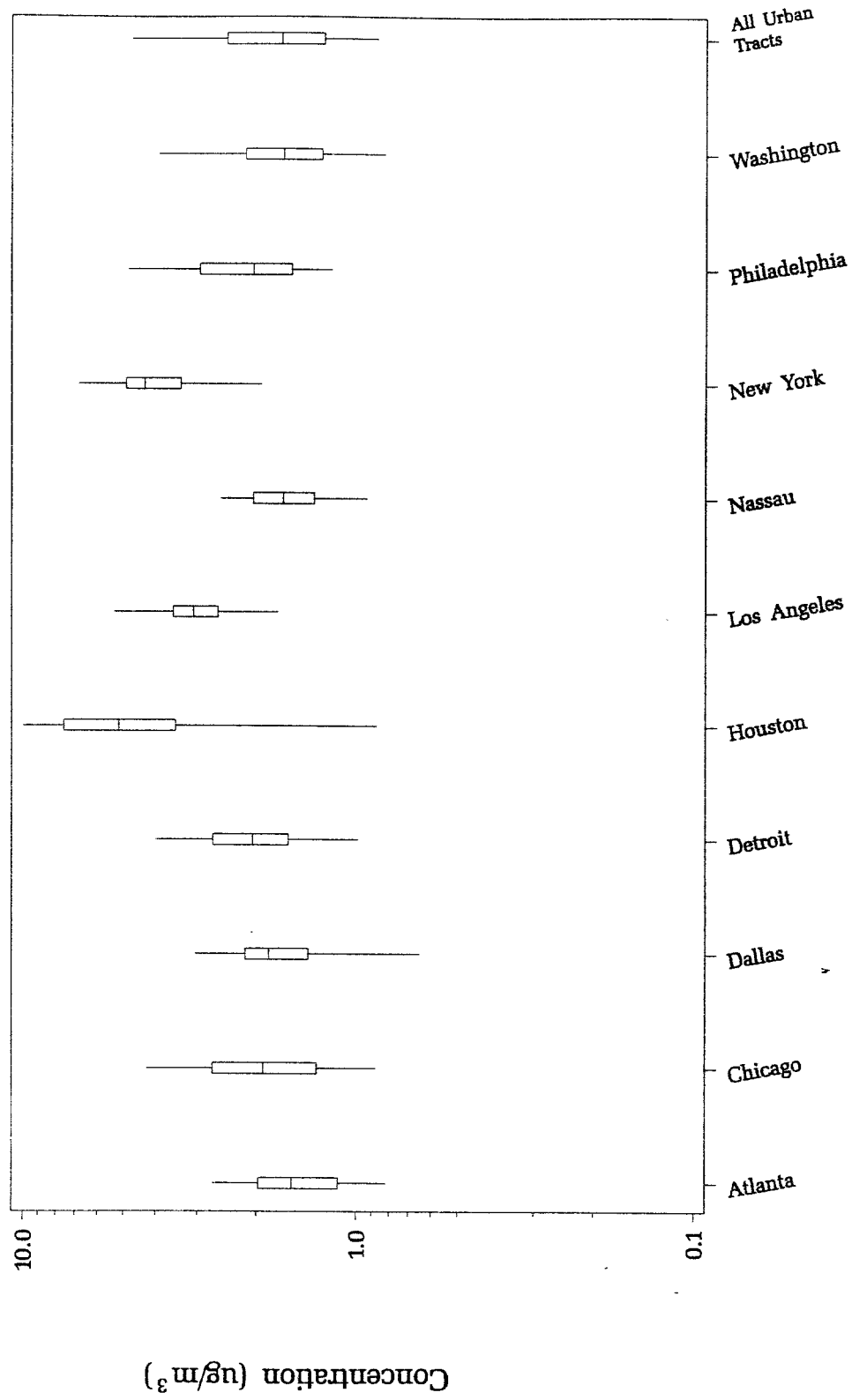


Figure 6-7
Distributions of Predicted Hydrazine Concentrations
Among Census Tracts

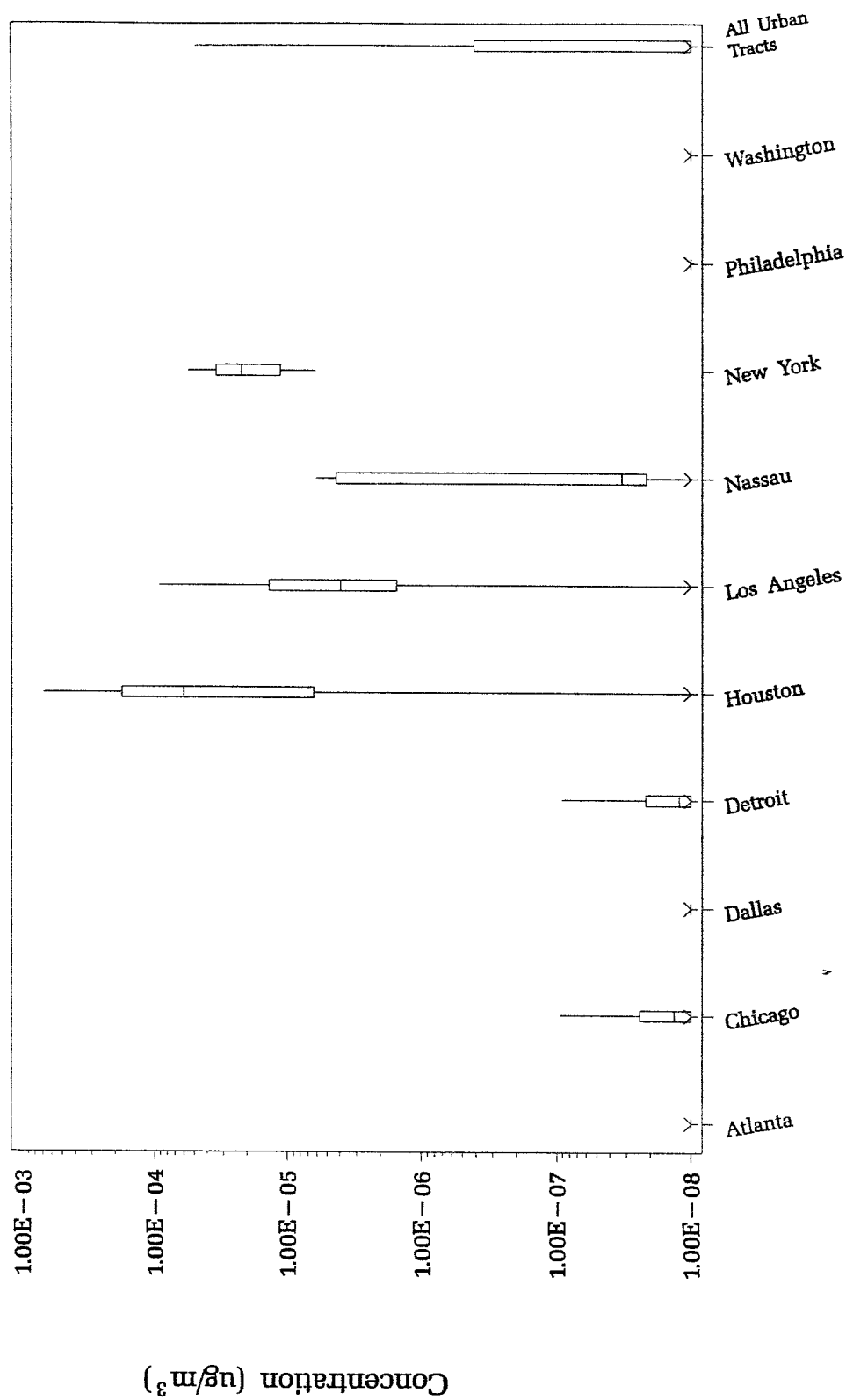


Figure 6-8
Distributions of Predicted MDI Concentrations
Among Census Tracts

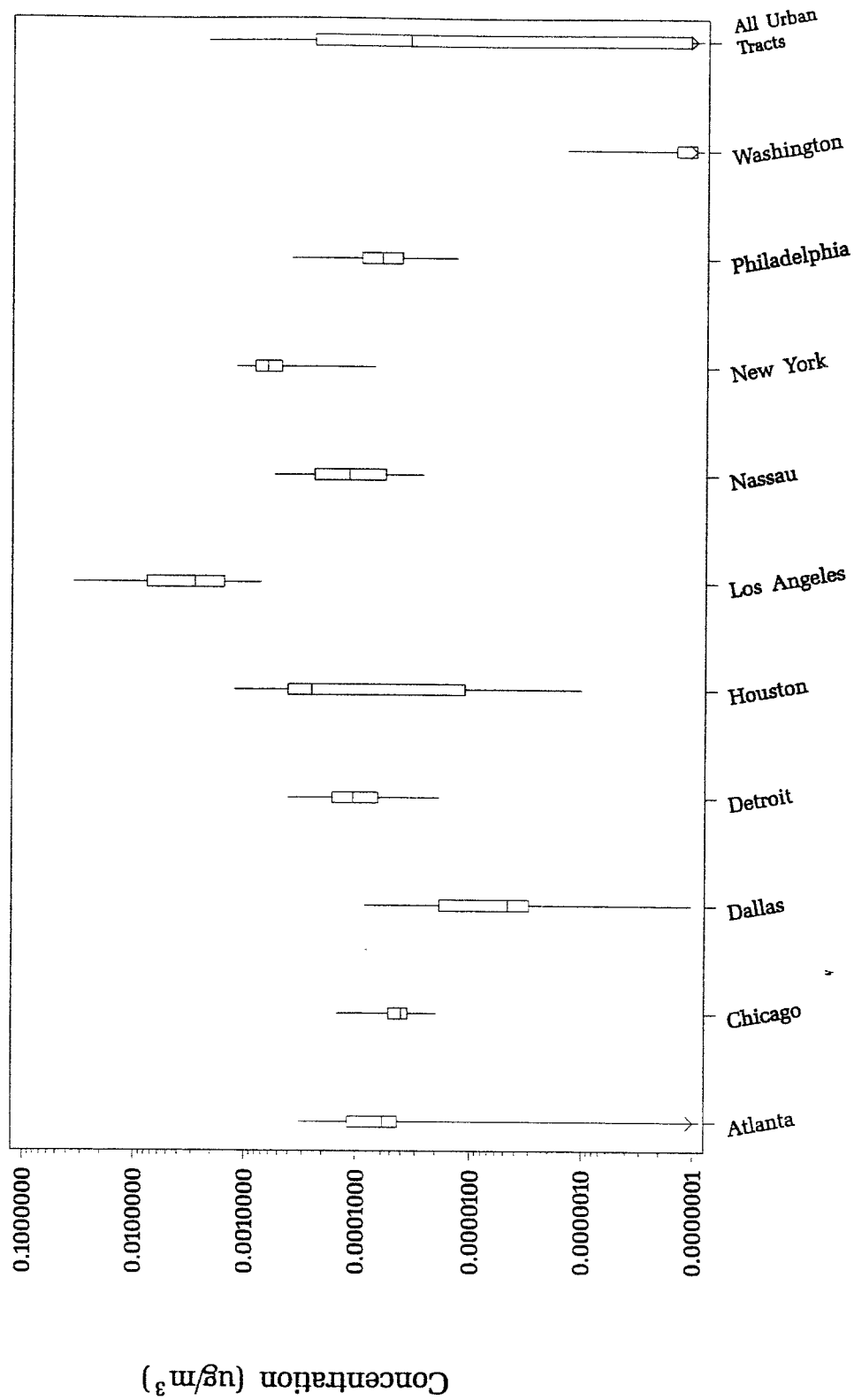
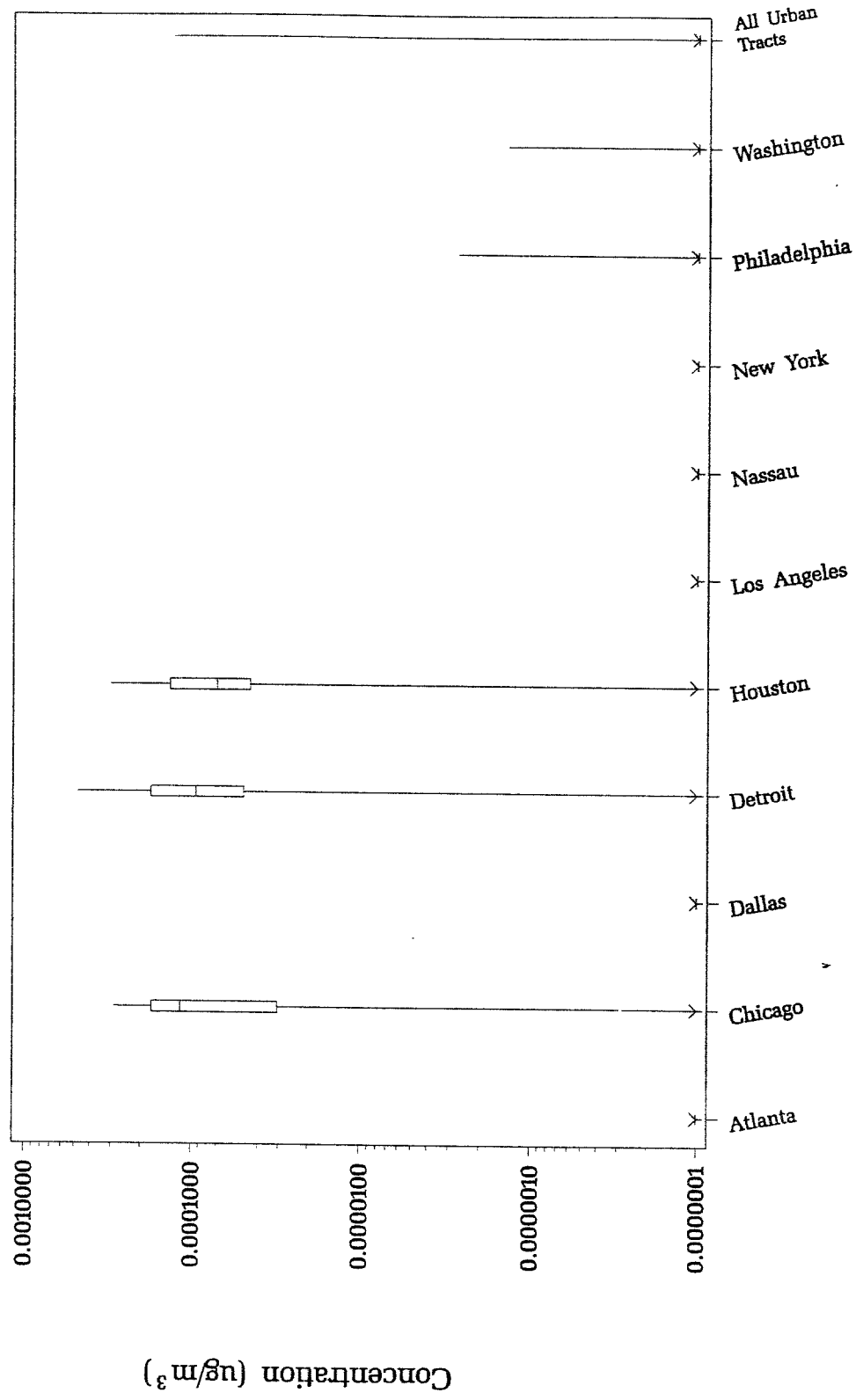


Figure 6-9
Distributions of Predicted Quinoline Concentrations
Among Census Tracts



7 MODEL PERFORMANCE EVALUATION

This chapter presents a summary of the ASPEN model performance evaluation. A detailed discussion is presented in Attachment 5. The model performance evaluation is focused on two key issues: (1) accuracy of the absolute magnitudes of predicted HAP concentrations, and (2) accuracy of the relative magnitudes of HAP concentrations among geographic areas. The first issue is addressed by examination of distribution of the ratios of predicted annual average concentrations to observed values, and the second by analyses of relative rankings described below.

EVALUATION METHODS

To evaluate the accuracy of the absolute magnitudes of predicted HAP concentrations long-term HAP measurement data were collected. For each observation, a predicted to observed (P/O) ratio was calculated. The distribution of P/O ratios was examined to see if the model results were unbiased (average ratio equal to 1), or tended to under- or over-predict (average ratio less than or greater than 1).

In order to account for the possibility that a pollutant monitor may be nearly equidistant from multiple census tracts, measured concentrations were compared with a distance-weighted average of the nearest six tract concentration predictions, weighting each value by $[\text{distance}]^2$ between the monitor and the tract centroid. As discussed in Chapter 5, ASPEN algorithms are designed to estimate concentrations that represent the average throughout the census tract. Although the HAP monitored values are point measurements, they are typically made in locations where concentration gradients are not expected to be steep, because the long-term monitoring programs from which they are taken are intended to represent general population exposures.

In addition to comparisons of annual average concentrations between ASPEN model predictions and observations for targeted HAPs, comparisons were made for carbon monoxide (CO). Although CO is not a HAP, it is included in the model simulations specifically for model evaluation purposes, because the CO measurement data base contains significantly more monitoring sites than the HAP measurement data base. In addition, CO is measured hourly throughout the year, whereas HAP measurements are typically 24-hour averages taken approximately every twelfth day. The greater temporal coverage reduces uncertainty in annual average statistics, and allows for time-of-day comparisons.

CO concentrations are known to vary seasonally, with the highest concentrations typically occurring in the winter, due to nighttime stagnation episodes during which CO concentrations build up over periods of several hours. To assure that annual averages of observed data are not biased due to missing data that may result in disproportionate seasonal representation, monitors with data for less than 75 percent of all days were omitted, and arithmetic averages were calculated as the mean of four seasonal averages.

Because one of the goals of this study is to compare concentrations of HAPs among geographic areas, the model evaluation includes an analysis of the accuracy of ASPEN

predictions with respect to the relative ranking of census tract concentrations. This was investigated with a statistic essentially equivalent to Kendall's tau. This statistic was constructed by calculating the proportion of site pairs where the ASPEN predicted concentrations are in the same order as the observed concentrations. These comparisons were made for all of the pairwise combinations of sites, as well as for subsets with concentration predictions that differ by factors of 1.5, 2.0, and 3.0. The results of this analysis indicate the probability of an accurate prediction about the relative ranking of a pair of census tract concentrations as a function of the percentage difference in predicted concentrations.

If there are systematic differences between observed data sets, due to differences in sampling and analysis techniques, combining them will introduce uncertainty into the observed relative rankings. The result could be a reduction in measures of ranking accuracy due to uncertainties in the observed data rather than uncertainties in the predicted data. Therefore, for the analysis of relative ranking, observed data sets have not been combined.

MONITORING DATA

Monitoring data of carbon monoxide (CO) and HAPs were obtained for model performance evaluation. CO data from 259 monitoring sites were extracted from EPA's Aerometric Information Retrieval System (AIRS) for comparison with ASPEN predictions. In selecting the sites, an attempt was made to eliminate those monitors identified as microscale or middle-scale and/or as maximum concentration or source-oriented. Because microscale and source-oriented monitors are located in order to detect extreme concentrations, or "hot spots", they are likely to record concentrations that are significantly higher than the ASPEN estimates for the corresponding census tracts, which represent tract averages. However, not all monitor records contained these identifiers, and some are likely to be incorrectly identified. Therefore, a certain amount of underprediction of CO concentrations is expected.

Comparisons of 1990 annual average ASPEN model predictions with observed HAP concentrations were made for eight monitoring programs: the California Air Resources Board Ambient Toxics Network (20 sites), the San Francisco Bay Area Air Quality Management District (15 sites), California's South Coast Air Quality Management District (4 sites), Maryland Department of Natural Resources (5 sites in Baltimore), the Staten Island/New Jersey Urban Air Toxic Assessment Project (3 sites), New York State Ambient-Toxic Air Monitoring Network (10 sites), Houston Regional Monitoring Corporation and South East Texas Regional Planning Commission (12 sites), and the Urban Air Toxics Monitoring Program (12 sites). Some of the programs were not operating in 1990, so that data for other years between 1988 and 1992 was used for comparison, introducing some uncertainty into the comparisons. Altogether 736 observations of 19 HAPs from 81 locations were used for comparison. HAP data sets with more than 10 percent of values below the minimum detection level were not used.

PREDICTED-TO-OBSERVED CONCENTRATION RATIOS

The accuracy of the absolute magnitudes of predicted HAP concentrations was evaluated by examination of ratios of predicted annual average concentrations to observed values for both CO and HAPs.

Carbon Monoxide. The P/O ratios of annual average CO concentrations for the 259 CO monitoring sites are approximately lognormally distributed, with values ranging from 0.12 to 1.81. The geometric mean ratio is 0.46, and the geometric standard deviation is 1.59 (see Table 7-1). Note that an assumed CO background concentration of 125 ppb has been added to the sum of predicted anthropogenic contributions to CO concentrations for this comparison. This value is based on 1989-1990 measurements at Niwot Ridge, CO (Novelli et al., 1992), a remote land site at approximately intermediate US latitude (40N). The geometric standard deviation of 1.59 suggests 95 percent confidence bounds of about plus or minus a factor of 3 for CO model predictions.

TABLE 7-1. Summary statistics of ratios of ASPEN 1990 concentration predictions to monitored annual average concentrations for carbon monoxide and selected HAPs.

Pollutant	Number of observation s	Geometric mean of ratios	Geometric standard deviation of ratios
Carbon Monoxide			
<i>Predictions compared to:</i>			
Observed arithmetic means	259	0.46	1.59
Observed arithmetic means ¹	100	0.56	1.50
Observed geometric means ¹	100	0.63	1.50
Observed daytime geometric means ^{1,2}	100	0.74	1.52
HAPs			
Acetaldehyde ³	32	0.36	2.04
Benzene	81	0.69	1.92
1,3-butadiene	20	0.28	1.69
Carbon tetrachloride	63	1.03	1.42
Chloroform	28	0.60	1.61
Dichlorobenzene (p)	25	0.19	2.59
Ethylbenzene	24	0.50	2.02
Formaldehyde ³	34	0.73	2.30
Hexane	2	1.27	1.55
Methanol	4	0.14	2.03
Methyl chloride	5	1.03	1.15
Methyl chloroform	70	0.79	2.27
Methylene chloride	29	0.20	2.22
Styrene	25	0.10	2.89
Tetrachloroethylene	67	0.41	2.80
Toluene	81	0.48	2.08
Trichloroethylene	47	1.02	4.34
2,2,4-trimethylpentane	9	0.80	1.82
Xylene	61	0.49	2.12
OVERALL	707	0.52	2.67

¹ Subset of monitors positively identified not related to "hot spots".

² Averages calculated for 6am to 9pm period only.

³ Because of the limitations of sampling technology, the observed concentrations of aldehydes may be underestimated (see discussion in text).

The results suggest that there is a systematic underestimate in the ASPEN predictions. There are a number of potential causes of this systematic underprediction:

- As noted above, although an effort was made to eliminate microscale/middlescale or “hot spot” monitors from the data set, it is likely that some of such monitors remain. Because the ASPEN concentration estimates are designed to represent the population-weighted average concentration over the census tract, these estimates would be expected to be lower than observed values at “hot spots”.
- Mobile source CO emissions may be systematically underestimated. Eighty-three percent of CO emissions come from mobile sources (67 percent from onroad sources, 16 percent from nonroad sources).
- Extreme meteorological events, such as stagnation (i.e., extended calm winds), that result in high concentrations are not treated by ASPEN. Because the Gaussian formulation cannot evaluate dispersion with calm wind speeds, such conditions are assumed to fall into the lowest wind speed category, 1 to 3 mph. The resulting concentration predictions are expected to be underestimates of observed values.
- Stable atmospheric conditions that may occur at night are poorly represented in the Gaussian formulation, because (1) concentration distributions for each time block are estimated independently, so that emissions that may carry over from one time block to the next during periods of low wind speed are not considered; and (2) highly nonstationary and inhomogeneous diffusive atmospheric processes that cause frequent aperiodic breakdowns of the stable boundary layer (Mahrt, 1985; Gossard et al., 1985; Nappo, 1991), are not captured.
- Concentrations are tracked to downwind distances of only 50 kilometers from the emission source, in accordance with EPA recommendations for Gaussian models. For concentration estimates at longer-range transport distances, an approach should be followed that addresses large-scale dispersion associated with three-dimensional wind fields, which is beyond the scope of this project.

To investigate the extent of influence from these potential causes, a number of alternative comparisons were made, and are discussed in Attachment 5. Re-analysis with a subset of 100 CO monitors that were positively identified as not related to “hot spots” showed higher average P/O ratios (see Table 7-1), suggesting that some of the unidentified monitors may be microscale or middle-scale monitors. However, even accounting for that possibility, there still appears to be a significant general underprediction.

The national Interim CO Emission Inventory (EPA 1993a), from which CO emissions were derived for this study, was developed using the December 4, 1992 version of MOBILE5. Considering the uncertainty in a number of factors that influence CO emission factors, discussed in Attachment 5, it is likely that MOBILE5 CO emission factors are reasonably accurate, but may be somewhat underestimated, probably by less than 25%. Although additional uncertainty in CO emissions estimates in the national Interim CO Emission Inventory would be contributed by uncertainty in vehicle miles traveled (VMT), overall the CO emissions would be expected to be reasonably accurate.

To the extent that underpredictions are the result of the modeling predictions neglecting high concentrations associated with extreme meteorological events, such as extended periods of calm, the predictions might be expected to match the annual geometric means of the observed values better than the arithmetic means. Although an analysis presented in Attachment 5 found this to be the case (see Table 7-1), large residual discrepancies suggest

that other factors besides neglect of extreme meteorological events are influencing the underestimates.

To investigate the contribution of nighttime predictions to the underestimates, comparisons were made between ASPEN estimates and observed measurements (geometric means) for daytime hours only (6 am to 9 pm), and a significantly better match was found (see Table 7-1). Figure 7-1 shows the comparison of predicted and observed annual average CO concentrations for daytime hours at the 100 monitors positively identified as not being related to "hot spots". However, significant discrepancies remain, suggesting the influence of additional factors.

Because significant discrepancies remain, the contribution of the 50 kilometer downwind distance limitation to the underestimates was investigated by examination of the daytime P/O ratios for the 70 California monitoring sites. Mean ratios for counties that are approximately 80 to 100 kilometers downwind from more populous areas were found to be lower than the California average, in contrast to upwind counties with higher than average mean ratios. This suggests that a significant portion of the underestimate may be due to the 50 kilometer downwind distance limitation.

HAPs. Table 7-1 also summarizes P/O concentration ratios for all HAPs for which a significant amount of monitoring data above the minimum detect level were identified. For these comparisons, the predicted annual average concentration is compared to the annual arithmetic mean observed concentration. All available observed data from the monitoring programs discussed above were combined for each HAP. The results for these HAPs show a pattern similar to that observed for CO, with geometric mean ratios generally less than 1.0, ranging from 0.10 to 1.27.

Among the gaseous HAPs, the geometric standard deviations of the ratios are approximately 2 or less, with the following exceptions: p-dichlorobenzene, styrene, tetrachloroethylene, and trichloroethylene. A geometric standard deviation of 2 suggests 95 percent confidence bounds of about a factor of 4 for model predictions.

Overall for all 19 HAPs combined, the geometric mean of the P/O ratios is 0.52, with 73% of the ratios lower than 1.0. This finding supports the conclusion drawn from the CO comparisons that the model has a general tendency to underpredict concentrations. Overall about half of the predictions are within a factor of 2 of the observations, and about 70% are within a factor of three.

Sampling of carbonyls (e.g., acetaldehyde and formaldehyde) by sorbent cartridges is known to be subject to "breakthrough" losses, often resulting in a low bias for concentration measurements. The situation is further complicated by the lack of NIST-gas phase standards for equipment calibration. The California Air Resources Board has recently determined that, due to "breakthrough", their 1990-1995 aldehyde measurements very likely underestimate ambient concentrations by an unknown amount. This is likely to be true of aldehyde measurements from other sampling programs as well. However, if the P/O ratios for acetaldehyde and formaldehyde are excluded, the overall statistics for the P/O ratios for the remaining 17 HAPs are virtually unchanged: geometric mean of 0.51, 73% of the ratios smaller than 1.0, about half of observations within a factor of 2 of the observations, and about 70% within a factor of 3.

Figure 7-2 shows the comparison of predicted and observed concentrations of 13 HAPs for the 5 monitoring sites in Baltimore. The results suggest that the model performs reasonably well in predicting the differences in concentrations among HAPs.

Emissions Uncertainty. A discrepancy between the predicted concentration at any location and the true concentration (represented by the observed concentration) results primarily from two types of uncertainty: emissions uncertainty and dispersion uncertainty arising from modeling limitations¹. That is,

$$\begin{aligned}\text{Observed conc(HAP, loc X)} &= \text{Emissions(HAP)} \times \text{Dispersion-factor(loc X)} \\ \text{Predicted conc(HAP, loc X)} &= \text{Est-emissions(HAP)} \times \text{Est-dispersion-factor(loc X)};\end{aligned}$$

so that

$$\begin{aligned}\text{Pred(HAP,loc X)/Obs(HAP,loc X)} &= \\ &= \frac{[\text{Est-emissions(HAP)/ Emissions(HAP)}] \times}{[\text{Est-dispersion-factor(loc X)/ Dispersion-factor(loc X)}]}\end{aligned}$$

If it is assumed that CO emissions estimates are reasonably accurate, and the observed CO data is not from a microscale or middle-scale monitor, discrepancies in P/O ratios for CO would represent primarily dispersion uncertainty. That is,

$$\begin{aligned}\text{Pred(CO,loc X)/Obs(CO,loc X)} &= \\ &= \frac{[\text{Est-emissions(CO)/ Emissions(CO)}] \times}{[\text{Est-dispersion-factor(loc X)/ Dispersion-factor(loc X)}]} \equiv \\ &= [\text{Est-dispersion-factor(loc X)/ Dispersion-factor(loc X)}]\end{aligned}$$

If it assumed that dispersion uncertainty for gaseous HAPs is the same as the dispersion uncertainty for CO at the same location, this information can be used to separate the dispersion uncertainty from the emissions uncertainty for a gaseous HAP at location X, as follows.

$$\begin{aligned}[\text{Pred(HAP,loc X)/Obs(HAP,loc X)}] \div [\text{Pred(CO,loc X)/Obs(CO,loc X)}] &= \\ \text{Est-emissions(HAP)/Emissions(HAP)}\end{aligned}$$

Thus, this "CO-adjusted" P/O ratio is an approximation of the ratio of the estimated emissions to the actual emissions in the vicinity of the monitor, i.e., an indication of the emissions uncertainty. For example, a ratio of 1.5 implies that the HAP emissions estimate in the vicinity of the monitor is approximately 50 percent higher than the actual emissions,

¹ Some of the discrepancy may also result from the difference in scale of representation between the monitored data and ASPEN model predictions, designed to represent a population-weighted average concentration over an entire census tract. If a monitor is located very near a large emission source, the observed concentration may not be representative of an area as large as a census tract. An attempt was made to omit such monitoring data from this study, but proximity to emissions sources was not always known.

and a ratio of 0.70 implies that the estimate is approximately 30 percent lower than actual emissions.

Table 7-2 presents summary statistics for "CO-adjusted" P/O ratios. The "CO-adjusted" P/O ratios are calculated using the closest CO monitor to each HAP monitor. For the HAP monitors used in this model performance evaluation, the distance from the nearest CO monitor ranges from 0 to 413 km, with a 90% interval ranging from 0 to 160 km, and a median distance of approximately 6 km. However, the bulk of the dispersion uncertainty is likely to be the result of the factors discussed above: extreme meteorological conditions, nighttime stagnations, and neglected medium-range transport. All of these phenomena occur at relatively large spatial scales, so the dispersion uncertainty should be similar for the majority of the HAP and CO monitor pairs.

TABLE 7-2. Summary statistics of "CO-adjusted" ratios of ASPEN 1990 concentration predictions to monitored annual average concentrations for selected HAPs.

Pollutant ¹	Number of observations	Geometric mean of ratios	Geometric standard deviation of ratios
Benzene	81	1.34	1.64
1,3-butadiene	20	0.78	1.52
Dichlorobenzene (p)	25	0.46	1.98
Ethylbenzene	24	0.74	1.93
Hexane	2	2.25	2.26
Methanol	4	0.13	2.03
Methyl chloroform	70	1.60	2.08
Methylene chloride	29	0.47	1.74
Styrene	25	0.26	2.14
Tetrachloroethylene	67	0.88	3.00
Toluene	81	0.92	1.98
Trichloroethylene	47	2.07	4.28
2,2,4-trimethylpentane	9	0.98	2.20
Xylene	61	0.88	2.12
OVERALL	545	0.95	2.64

¹ "CO-adjusted" P/O ratios were not calculated for carbon tetrachloride, chloroform, and methyl chloride, because the predicted concentrations of these HAPs are dominated by background contributions, which are not subject to dispersion uncertainties. Similarly, "CO-adjusted" P/O ratios were not calculated for acetaldehyde and formaldehyde, because they have significant secondary components for which dispersion is likely to be quite different from CO.

The results suggest that emissions of *p*-dichlorobenzene, methanol, methylene chloride, and styrene may underpredicted by more than a factor of two ("CO-adjusted" mean P/O ratio less than 0.50), indicating that significant sources may have been omitted from the emission inventory. In contrast, the "CO-adjusted" mean P/O ratio for trichloroethylene is 2.07, suggesting that emissions of this HAP are significantly overpredicted. Overall for all 14 HAPs combined, the geometric mean "CO-adjusted" ratio is 0.95, with about 49% of the ratios less than 1.0. Fifty-nine percent of the "CO-adjusted" P/O ratios are between 0.5 and 2.0, suggesting that predicted emissions are within a factor of 2 of actual emissions at those locations. More than 75 percent are between 0.33 and 3.0, suggesting emissions accuracy of a factor of 3.

RELATIVE MAGNITUDES OF CO AND HAP CONCENTRATIONS AMONG CENSUS TRACTS

The accuracy of the relative magnitudes of HAP concentrations among geographic areas was evaluated by examination of relative rankings compared to observed data.

Carbon Monoxide. The predicted/observed 1990 concentration pairs for the 259 monitoring sites show a frequency of ranking agreement between predicted and observed concentrations of 60 percent for all concentration pairs, and 68, 74, and 79 percent for pairs with predicted concentrations differences of at least a factor of 1.5, 2.0, and 3.0, respectively. The corresponding results for the subset of 100 monitors positively identified as not being related to "hot spots" are 65, 75, 82, and 88 percent, respectively. The results are nearly identical whether the predicted concentration ranking are compared with those of the arithmetic means of the observed values or the geometric means.

Selected HAPs. Table 7-3 presents the ranking statistics for HAPs from the four monitoring programs with the largest number of monitoring sites, for predicted concentration differences of at least a factor of 2.0. Ranking performance tends to vary by pollutant and monitoring program. The performance for the majority of the HAPs appears to be reasonably good for California Air Resources Board (CARB) monitoring sites. For example, for 8 of the 12 HAPs there is ranking agreement of 70 percent or more. The poorer matching of predicted and observed rankings for acetaldehyde and formaldehyde is notable, and may be related to the uncertainties in the measured concentrations. An additional factor may be that each of these HAPs includes significant contributions from secondary formation. Although ASPEN includes a simplified representation of secondary formation, as described in Chapter 5, it is likely to understate secondary contributions, due to the 50 km downwind distance limitation for tracking pollutant concentrations, past which much of the secondary formation is likely to take place. This indicator of model performance is also generally poorer for trichloroethylene, which was identified in the previous section as likely to have significantly overestimated emissions estimates.

TABLE 7-3. Frequency of ranking agreements¹ between modeled and monitored pollutant concentration values.

Pollutant	CARB	NY State	BAAQMD	HRM/SET	UATMP
Acetaldehyde ²	57%				55%
Benzene	63%	100%	96%	86%	79%
1,3-butadiene	71%				
P-dichlorobenzene	71%				
Ethylbenzene		100%			61%
Formaldehyde ²	49%				60%
Methyl chloroform	80%	91%	89%	36%	52%
Methylene chloride	79%				
Styrene	82%				
Tetrachloroethylene	82%	100%	68%		76%
Toluene	76%	100%	84%	95%	38%
Trichloroethylene	47%				
Xylene	72%	88%		100%	63%

¹Percentage of site pairs where ordering of modeled concentration values is the same as the ordering of monitored values, for those pairs in which modeled values differ by more than a factor of 2.

²Because of the limitations of sampling technology, the observed concentrations of aldehydes may be underestimated (see discussion in text).

Ranking performance for the NY State monitoring sites is good for all HAPs. Ranking performance for the San Francisco Bay Area Air Quality Management District program (BAAQMD) sites is as good or better for corresponding HAPs compared to performance for the CARB sites, with the exception of tetrachloroethylene. Ranking performance for the Houston Regional Monitoring/ South East Texas Regional Planning Commission Program (HRM/SET) monitors is better than for the CARB monitors for benzene, toluene, and xylene, but quite poor for methyl chloroform. Ranking performance for the Urban Air Toxics Monitoring Program (UATMP) sites is better than for the CARB sites for benzene and formaldehyde, but worse for methyl chloroform and toluene, and similar for the remaining HAPs. Note that because the UATMP sites are geographically dispersed, the handling of samples is unlikely to be uniform, introducing some uncertainty into the comparability of measurement values.

DISCUSSION

Comparison of model predictions with observed concentrations of carbon monoxide and selected HAPs suggest a tendency for underprediction. A number of limitations of the Gaussian model formulation that are likely to contribute to the underprediction have been discussed, such as neglect of calm wind conditions, poor representation of stable atmospheric conditions, and a 50 kilometer downwind distance limit. Uncertainties in the national HAP emission inventory may also explain a portion of the underprediction tendency.

The geometric standard deviations of P/O concentration ratios, presented in Table 7-1, range from about 1.2 to 2.3 for 15 of 19 HAPs evaluated, suggesting 95 percent confidence bounds ranging from a factor of less than 2 to about 5 for model estimates. The estimates of emissions uncertainty for 14 HAPs presented in Table 7-2 suggest that half are within a factor of 1.5, and almost 80% are approximately within a factor of 2, on average.

In spite of a tendency for underprediction, results may be used to compare HAP concentrations among geographic areas if the relative ranking of concentration predictions are reasonably accurate. The frequency of agreement in ranking between predicted concentrations and those observed in the various HAP monitoring program suggests reasonably good performance for most of the primary HAPs when predicted concentration differences are large, with the exception of trichloroethylene. Given the uncertainties in the model predictions, small differences in model estimates should probably not be considered in making comparisons across sites.

The match of predicted and observed rankings of the selected HAPs with significant secondary components (i.e., formaldehyde and acetaldehyde) is poorer. This may be due to uncertainties in the measured concentrations and/or to the 50 kilometer downwind distance limitation of the Gaussian modeling formulation.

The findings of the model performance evaluation are also useful for highlighting where improvements can be made in the modeling methodology. Supplementary estimates of concentration contributions from sources more than 50 kilometers away might improve performance, especially with respect to secondary formation. This would require modeling that accounts for large-scale dispersion associated with three-dimensional wind fields.

The findings also highlight where there is greatest uncertainty in the national HAP inventory. For example, the emissions uncertainty analysis suggests that that significant sources of *p*-dichlorobenzene, methanol, methylene chloride, and styrene may be absent from the emission inventory, while emissions of trichloroethylene may be significantly overestimated. However, the number of observations of methanol is small.

Figure 7-1
Carbon Monoxide
ASPEN predictions vs observed arithmetic means
Daytime Values

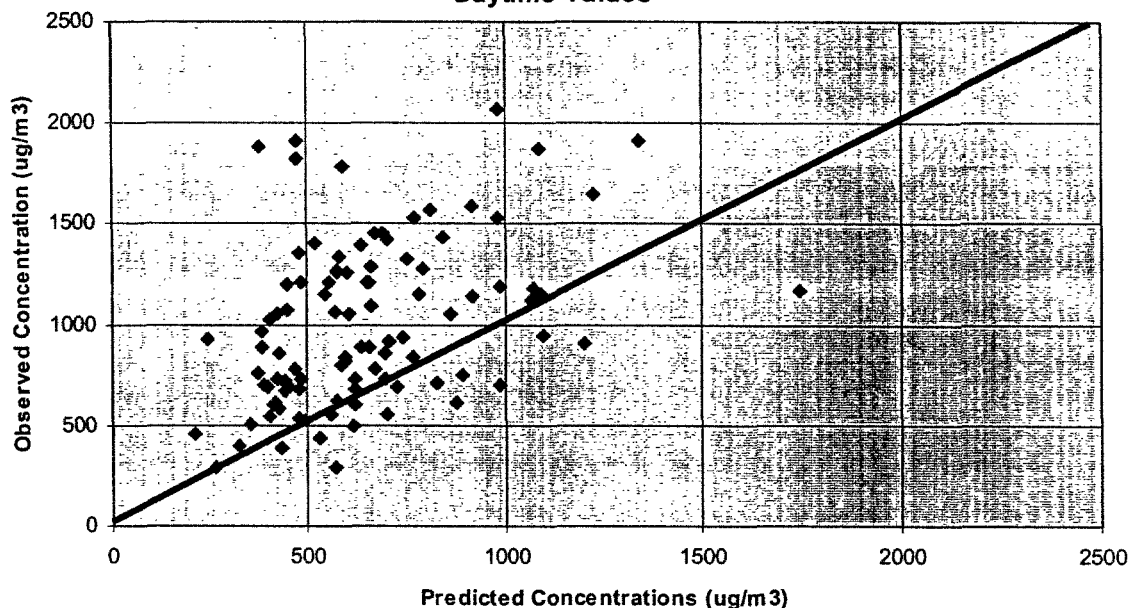
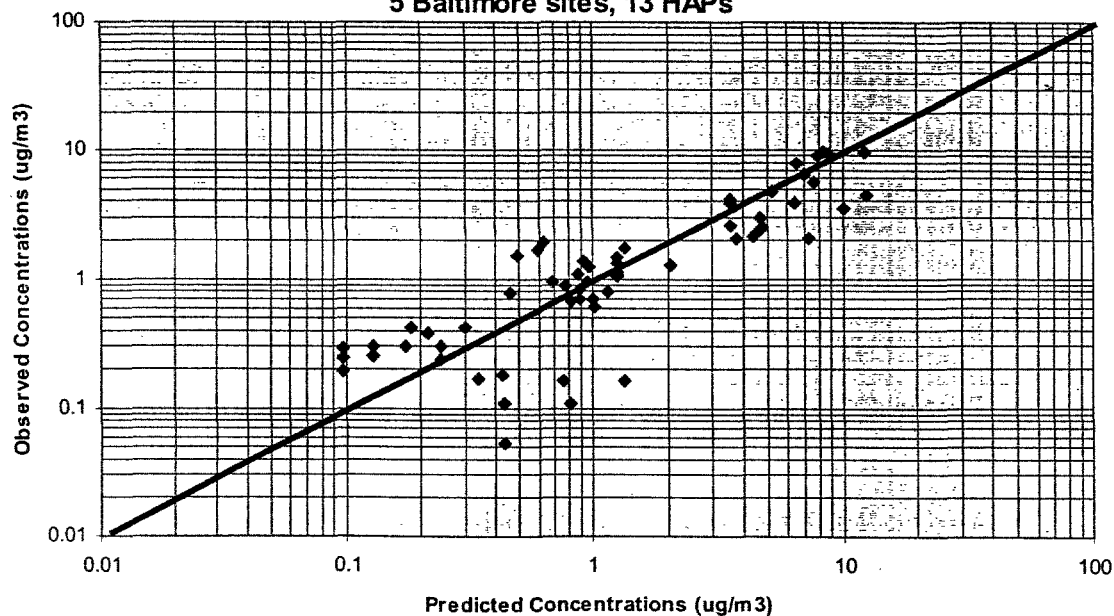


Figure 7-2
ASPEN predictions vs observations
5 Baltimore sites, 13 HAPs



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